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Carnegie Institute of Technology

Department of Physics



LUMINESCENT EFFICIENCY OF LARGE CRYSTALS OF CaWO_4 AND CeWO_4

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TABLE OF CONTENTS

List of Figures	iii
List of Tables	v
ABSTRACT	1
ACKNOWLEDGEMENT	2
I. INTRODUCTION	3
II. LUMINESCENCE OF INORGANIC NON-PHOTOCONDUCTING PHOSPHORS	4
<u>A. Basic Characteristics of Non-Photoconducting Phosphors.</u>	4
<u>B. The Luminescent Center</u>	8
III. EFFICIENCY MEASUREMENTS WITH POWDER AND SINGLE CRYSTAL PHOSPHORS	13
<u>A. Efficiency Measurements with Crystalline Powders</u>	14
<u>B. Efficiency Measurements with Slabs of Luminescent Materials</u>	16
IV. EXPERIMENTAL EQUIPMENT AND TECHNIQUES	25
<u>A. Description of Equipment Used to Determine the Spectral Distribution</u>	25
<u>B. Description of Apparatus Used for Efficiency Measurements</u>	32
<u>C. The Reflection and Transmission Equipment</u>	37
V. MEASUREMENTS ON CaWO_4 AND CdWO_4	38
<u>A. The Reflection Measurements at 2537 Å</u>	39
<u>B. The Transmission Measurements</u>	40
<u>C. The Luminescent Spectra Measurements</u>	43
<u>D. The Efficiency Measurements</u>	44
<u>E. Future Work on CaWO_4 and CdWO_4</u>	47
REFERENCES	49
FIGURES	51

LIST OF FIGURES

1. Typical Emission Spectrum and Temperature Dependence of a Non-photoconducting Phosphor	51
2. Energy vs. Configuration Curve for a Luminescent Center	52
3. Parameters Used in the Calculation of the Distribution of Luminescent Light Emitted From a Point in the Interior of a Slab.	53
4. Loci of Virtual Sources in CaWO_4	54
5. The First Three Terms of Eq. (7) and Their Sum Computed for Parameters Used in the CaWO_4 Calculation	55
6. Schematic Diagram of the Equipment for Obtaining a Luminescent Spectrum.	56
7. Schematic Diagram of the Equipment Arrangement for Calibrating the Spectrometer Plate and its Associated Optics	57
8. Cross Section of the Cryostat Used to Maintain the Crystals at a Fixed Temperature	58
9. Spectral Distribution of the Lamp Used to Calibrate the Spectrum Determinations After Correcting for the Non-black Emissivity of Tungsten and for the Bulb Transmission	59
10. Examples of the Photographic Plates Used in Determining the Spectral Distribution	60
11. A Densitometer Tracing Obtained From the Spectrum Plate	61
12. An Example of the Curves Used to Analyze the Spectrum Plates	62
13. Photocell Circuit	63
14. Schematic Arrangement of Equipment Used to Calibrate the Photocell	64
15. Photocell Calibration Curve	65

16.	Schematic Arrangement of Apparatus for Efficiency Measurements .	66
17.	Reflection Measurement Equipment	67
18.	Reflection of 2537 A Ultraviolet from CaWO_4 Crystals	68
19.	Reflection of 2537 A Ultraviolet from CdWO_4 Crystals. The Dashed Line Connects Data from Different Parts of the Same Crystal	69
20.	Reflection of 2537 A Ultraviolet from the Part of the Surface of the CaWO_4 Crystals Used for the Efficiency Measurements	70
21.	Optical Transmission of CaWO_4 Crystals from 2100 A to 7200 A . .	71
22.	Optical Transmission of the CaWO_4 Crystals in the Cutoff Region Showing that Both Crystals Appear to have the Same Cutoff . . .	72
23.	Demonstration that all of the Photocell Response from CaWO_4 Crystal #2 Beyond the Cutoff is Due to Luminescence Excited by the Spectrophotometer Beam	73
24.	Transmission of CaWO_4 Crystal #1 Near 2537 A	74
25.	Transmission of CdWO_4 Crystals	75
26.	Detail of the CdWO_4 Transmission from 2000 A to 3500 A	76
27.	Detail of the CdWO_4 Transmission from 3000 A to 4500 A	77
28.	Luminescent Spectrum Measurements on CaWO_4 at Room Temperature .	78
29.	Luminescent Spectrum Measurements on CaWO_4 at Dry Ice Tempera- ture	79
30.	Luminescent Spectrum Measurements on CaWO_4 and Liquid Air Temp- erature Data.	80
31.	Luminescent Spectrum Measurements on CdWO_4 at Room Temperature .	81
32.	Luminescent Spectrum Measurements on CdWO_4 at Dry Ice Tempera- ture	82

33. Luminescent Spectrum Measurements on CdWO_4 at Liquid Air Temperature	83
34. Room Temperature CaWO_4 Spectra as Observed and Corrected to the Interior of the Crystals. The curves were Matched at the Peak . .	84
35. Temperature Dependence of the Luminescent Efficiency of Powdered CaWO_4 and Our Single Crystals	85
36. Temperature Dependence of the Luminescent Efficiency of Powdered CdWO_4 and Our Single Crystals	86
37. The Energy Conversion Data Which Shows the Linear Dependence of the Luminescence Emitted from CdWO_4 and CaWO_4 Single Crystals When Excited by 2537 A Ultraviolet Light	87

LIST OF TABLES

1. Energy Conversion and Quantum Efficiency of CaWO_4	45
2. Energy Conversion and Quantum Efficiency of CdWO_4	47

ABSTRACT

The problem of determining the luminescent efficiency of phosphors in the form of powders and large single crystals is considered. A method applicable to large single crystals has been developed and applied to crystals of synthetic CaWO_4 and CdWO_4 . As an adjunct to the efficiency measurements the luminescent spectra of these materials was measured at liquid N_2 , dry ice, and room temperatures. Also, their reflection of 2537 Å ultraviolet and optical transmission from 2100 Å to 8000 Å is given for room temperature. The room temperature quantum efficiencies of two different crystals of CaWO_4 are 0.74 and 0.82, in agreement with published values for the efficiency of powders. Due to large uncertainties in the indices of refraction, the efficiencies obtained for two crystals of CdWO_4 , 1.0 and 1.2, values that are probably too large, must be considered unreliable.

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THE LUMINESCENCE OF LARGE SINGLE CRYSTALS

OF CaWO_4 AND CdWO_4

I. INTRODUCTION

The electronic properties of insulators have received considerable attention in the last decade. Studies of semi-conductors, photoconductors, and luminescent materials have yielded detailed information about, for example, the energy difference between the filled and conduction band, the number and energy levels of trapping centers, the interplay between trapping centers and luminescent centers, some details about the luminescent centers, etc. Practically all of the experimental information on luminescence was obtained with crystalline powders. The small amount of information obtained from single crystals can be attributed to the fact that large single crystals were practically unobtainable, except for those occurring naturally, and these were of doubtful purity. One of the more important properties of phosphors is their efficiency, which roughly is the ratio of the energy they absorb to the energy they emit as luminescence. Very few reliable efficiency measurements exist even for powders, and these have inherent properties, of which the most important is their permanent entrapment of part of the luminescent light they emit, that limit the accuracy of the efficiency measurements. However, some of these difficulties do not arise with large single crystals primarily because they can be obtained as regular parallelepipeds for which one may calculate the fraction of light, produced in the interior of these crystals, that escapes from them. When large synthetic high purity crystals

of calcium and cadmium tungstate, which are both luminescent, became available the efficiency measurements, to be described here, were undertaken. The method developed for this purpose requires among other things a measurement of the spectral distribution of the luminescence, and the absorption and reflection of light of various wavelengths by the luminescent crystals. In addition to measuring these properties for all of the crystals used, the spectral distributions were measured at 78° K and 195° K as well as the ratios of the efficiencies at these temperatures to the efficiencies at room temperature.

II. THE LUMINESCENCE OF INORGANIC NON-PHOTOCONDUCTING PHOSPHORS

First let us outline the physical characteristics of luminescent crystals. Once we have done this we can introduce the concept of the luminescent center, an entity that will permit us to understand qualitatively a majority of the observed experimental facts.

A. Basic Characteristics of Non-photoconducting Phosphors

The experimental facts and current theories on the luminescence of inorganic solids are summarized in books by Garlick(1) and Leverenz(2) that have recently appeared. In addition, there is the report "Cornell Symposium on Luminescent Materials" edited by Fonda and Seitz(3), and books by Kröger(4) and Pringsheim(5). The latter two publications can be regarded as compendiums of experimental data, while the first three are devoted more to the current theories and mechanisms involved in the luminescent process.

There is no generally accepted terminology in this field and we will give the definitions that we will use of the most common terms. In its

simplest form luminescence is the absorption of light by a substance and its subsequent reemission as light of lesser energy. In general, however, luminescence includes all those processes whereby energy is imparted to a substance with the ultimate release of some or all of this energy as light. Consider the following idealized experiment. Let a square wave of ultraviolet light fall on a typical luminescent material. At the onset of the ultraviolet the material will almost instantaneously luminesce, in addition a second component will grow in until the emitted light reaches a steady level. When the exciting ultraviolet is shut off the emitted light will sharply drop off with a time constant on the order of 10^{-8} to 10^{-2} seconds. This initial diminution will then be followed by a decaying component which may have a time constant ranging from a few milliseconds to several days! The fast rising and decaying component is usually called fluorescence and slower changing components are called phosphorescence. If only one component is present in a given material it can be called either fluorescence or phosphorescence if its time constant is on the order of 0.1 second or less. There is no generally accepted way to differentiate between the two and we shall refer to both processes collectively as luminescence. It has been shown that single crystal CaWO_4 is non-photoconducting and we will assume that in both CaWO_4 and CdWO_4 only one process is operating(6). Also, we will occasionally use the word phosphor for any luminescent material and when so doing we do not intend to imply anything about its phosphorescent characteristics.

With surprisingly few ambiguities all phosphors can be divided into photoconducting and non-photoconducting materials, i.e., if crystals of these materials are fitted with electrodes to which a potential is applied

some will permit a current to flow when they are illuminated with ultra-violet light while others will not permit a current to flow no matter how intense the incident light is. Since the crystals which were used in this investigation are of the non-photoconducting variety we will consider in detail the process involved in the luminescence of non-photoconducting materials and make only occasional reference to materials and mechanisms involving photoconductivity.

Practically all phosphors are highly crystalline and contain amounts of some impurity, called the activator, ranging from 10 to 10^{-4} atomic percent. In a few cases it is unambiguously known that the impurity is substitutional or that it is interstitial. While it is believed that in the majority of cases the impurity is substitutional this has not been definitely established. If one determines the absorption of the crystal without activation--the host crystal--and then the host to which an activator has been added, one can usually find an absorption band attributable to the activator alone. If one illuminates the activated crystal in this band one finds the luminescent emission is a broad band, e.g., Fig. 1, that lies entirely at the longer wavelength side of the absorption band. Now if one follows the decay of the emission after extinguishing the exciting radiation one finds that in most cases it decays exponentially. The rate of decay is often expressed in terms of a decay time, which is the time required for the emission to fall to $1/e$ of its original value. Usually if a phosphor is found to decay like t^{-n} where $1 < n < 3$ it will also be found to be photoconducting(1a), which we reiterate, is a type that will not be considered here.

In general the emission spectrum will have the slightly asymmetrical inverted bell-shaped curve shown in Fig. 1. With one exception the shape of the spectral distributions have not been derived from first principles. Later we will show why the shape of the emission spectra must be precisely known if an accurate determination of the luminescent efficiency is to be made.

The term, the luminescent efficiency, must be considered in detail before we proceed. If one imparts a given quantity of energy to a crystal phosphor system then all or part of this energy will ultimately be reemitted as luminescent light. We define the luminescent efficiency, or as we actually prefer to call it "the energy conversion,"

$$\eta = \frac{\text{energy emerging from phosphor as luminescent light}}{\text{total energy imparted to phosphor}}$$

For most cases, actually the only one we will use, the energy imparted to the crystal will be the amount of ultraviolet light it absorbs. Often "quantum efficiency" is the name given to this quantity, but this is incorrect, the proper definition of the η_q the quantum efficiency being

$$\eta_q = \frac{\text{number of quanta emitted by the phosphor as luminescence}}{\text{number of exciting quanta absorbed by the phosphor}}$$

It is important to note that these quantities refer to hypothetical measurements made in the interior of the crystal and when dealing with light exterior to the crystal certain corrections must be made. The most important of these results from reflections at crystal surfaces leading to permanent trapping of part of the luminescent light. If one knows the energy distribution of the exciting ultraviolet and of the emission spectrum one can compute the quantum efficiency from the energy conversion and

vice versa.

For the typical non-photoconducting phosphor it is usually found that the efficiency is strongly temperature dependent as is shown in Fig. 1, but the decay time, and the shape of the emission spectra are independent of temperature in the range of 80° K to 300° K. Also, one can vary the wavelength of the exciting ultraviolet. In this way one determines that the exciting photons must possess a minimum critical energy before any emission is observed. It is customarily found that the efficiency varies strongly with the energy of the excitation but that the emission spectra, if it is observed at all, does not depend on the energy of the excitation.

B. The Luminescent Center

In the previous section we have outlined the principle characteristics of luminescent materials. The first successful attempts to assimilate this information into a coherent picture was made by Seitz(7) and Von Hippel(8). The picture they formulated is best applied to an impurity activated phosphor. Consider a substitutional impurity in its host lattice. This foreign atom and the atoms surrounding it may be regarded as a kind of molecule which is called a luminescent center. The center must possess an electric ground state (level) and at least one excited state. To one, or perhaps more, of the electrons in this center one may ascribe a potential energy diagram, like that of Fig. 2, where energy is plotted vertically and the abscissa is called the configuration coordinate for want of a more precise name. If this diagram were applied to a molecule the configuration coordinate would be the nuclear separa-

tion. Actually, in the luminescent center, this coordinate is an average over $3N$ deviations from a mean position, where N is the number of nuclei and electrons that must be considered part of the center. Just recently Williams(9) has calculated curves like these for the case of thallium activated KCl and obtained fairly good agreement with experimental absorption and emission spectra thus lending credence to the postulates of Von Hippel and Seitz.

It must be emphasized that while this diagram refers to electronic states the vibrational states of both the solid as a whole and the luminescent center separately must be superimposed on the electronic part. This vibrational part is suggested by the light horizontal lines drawn in each curve. Actually there are many more vibration levels than indicated. An important characteristic of these centers is that an electron in any of the higher vibrational levels will degrade to the bottom of each electronic level. Moreover, an electron at the bottom of each level will undergo thermal fluctuation to some of the higher levels. This property must be exploited to explain the temperature dependence of the quantum efficiency. Consider now the absorption of light by a phosphor which contains luminescent centers. The center will usually be in the ground state, such as the point A in Fig. 2, especially if the energy W is large compared to kT . In order that the optically active electron of the center be raised to the upper level it must absorb a quantum having energy W or greater. This explains why only sufficiently energetic light excites luminescence.

Once the center is raised to the upper level, such as the point D,

it will undergo thermal degrading to the point B. There are two alternatives as to how the electron may return to the ground state from this point. Suppose that E is much larger than kT so that there is only small probability that the electron may reach the point C by the normal thermal fluctuation process. It will then remain in the excited state until it makes an optical transition to the ground state with the emission of a photon. Thus the optical transition controls the decay time of the phosphor. We know of no successful attempts to calculate the transition probability from first principles.

From the details of the emission process the qualitative features of the broad emission spectra can be described. The electron in the upper state will not be precisely at the bottom of the curve since it will have some zero point energy and, in addition, will possess some thermal vibration energy. Thus, in terms of the potential energy diagram it is in a state indicated by one of the fine lines above the point B. Now it can make an optical transition from any point on this line, i.e., it can make an optical transition independently of its degree of thermal motion, to any point on the curve describing the lower state. Obviously, there is a large number of such transitions which when properly weighted can account for the broad spectral distribution of the emission spectra. An exact inverse of this mechanism, the raising of an electron from the lower to the upper state, accounts for the observed absorption. The results of Williams match the observed spectral distribution well enough so that there is no doubt that we have correctly described the first order features of these processes.

Von Hippel and Seitz postulated that the two curves representing the excited state and the ground state must cross. In Fig. 2 this point is labeled C. This makes it possible to explain the dependence of the luminescent efficiency on the temperature. Assume that the center is in the state B. There are two processes whereby it may return to the ground state of which the first is the optical transition we have just discussed. The second process, which competes with the optical transition, occurs when the center is thermally excited (subjected to a thermal fluctuation) sufficient to raise it to C. The electron may then pass to the lower curve, perhaps with the emission of an infra-red quantum, and be degraded to A the lattice absorbing the phonons emitted in this process.

Let b be the probability that the center undergoes an optical transition from B. The probability that the center, in the excited state, reaches the point C is

$$p_0 e^{-E/kT}$$

where k and T have the usual meaning and E is the energy separating B and C. p_0 is sometimes called the "attempt to escape" frequency and ranges from 10^6 to 10^{13} for different materials. The quantum efficiency η_q is then

$$\begin{aligned} q &= \frac{\text{probability of an optical transition}}{\text{total number of events}} \\ &= \frac{b}{b + p_0 e^{-E/kT}} = \frac{1}{1 + p e^{-E/kT}} \end{aligned} \quad (1)$$

$$\text{where } p = p_0/b$$

This expression is curve 1 in Fig. 1(b). It has been found that for powdered CaWO_4 , excited by 2400 Å ultraviolet, the dependence of η_q on T is given exactly by this formula. However, if 2537 Å excitation is used the agreement is not good(4a). At very low temperatures, the experimental points fall below the theoretical curve as is shown in curve 2 of Fig. 1(b). This is another point for which there is no generally accepted explanation.

It is to be noted that one may fit equation (1) to the experimental data giving the variation of η with T by adjusting p and W without knowing the absolute value of η_q . One of the primary concerns of this investigation is the determination of an absolute quantum efficiency η_q for large crystals of CaWO_4 and CdWO_4 .

Before proceeding to the details of such a determination we must clear up one point about the CaWO_4 and CdWO_4 crystals we will use. When this work was started these materials were the only crystals that could be obtained sufficiently large to make the method to be used applicable. The precise mechanism for their luminescence is not known. There are two possibilities that merit consideration. These crystals could be self-activated(2a), that is, they could contain stoichiometric excesses of one of their constituents, most probably tungsten. The self-activator could be either interstitial or substitutional. The other explanation(4a), (1b) arises from the fact that in both of these crystals, as well as other tungstates that are luminescent, the tungstate groups are closely coordinated, the tungsten atoms being tetrahedrally surrounded by the four oxygen atoms(10). There is no known reason why a WO_4 coordinate group

cannot have the properties of a luminescent center and the observed luminescence be an inherent property of the material. One fact that supports this supposition is that a great many tungstates that are luminescent have different crystal structures, but in every case the WO_4 is present as a coordinate group. In addition, the luminescent spectra of these materials are all similar.

III. EFFICIENCY MEASUREMENTS WITH POWDER AND SINGLE CRYSTAL PHOSPHORS

The phrases luminescent efficiency, or energy conversion, and quantum efficiency have been carefully defined. The process of measuring these quantities must also be carefully considered. This has been done in a general way by Leverenz(2b) but for this investigation we must examine certain details. Allow a phosphor, either a single crystal or crystalline powder to be excited by monochromatic ultraviolet light. At the surface of the material a fraction of the incident light will be reflected and the remainder will enter the crystal according to the principles of classical optics, e.g., see Jenkins and White(11). The entering light will be absorbed by the luminescent centers, by the host crystal, by impurities, or by some combination of them. Since the crystal is luminescent some of the energy absorbed will be reemitted by the luminescent centers. This emission, which will have a broad spectral distribution, can be entirely or partially absorbed by the host lattice, and that part which is not absorbed will be reflected and refracted by the crystal surface before it can emerge from the crystal. The amount of emitted light that emerges, will depend on the index of refraction and the geometric shape of the crystal. We will consider the case of cryst-

alline powders and, in more detail, the case of a large single crystal.

To relate the quantum efficiency to the luminescent efficiency, or energy conversion, requires a knowledge of the spectral distribution of the emitted spectrum particularly if the detector, e.g., a photo cell, is not completely black. And, since the spectrum must be measured external to the crystal we must be able to calculate the spectrum we would observe if we could measure it internally. Unless the crystal absorbs a large fraction of the luminescence internally the observed spectrum will differ only slightly from that emitted by the centers.

A. Efficiency Measurements with Crystalline Powders

The surface presented to exciting ultraviolet by a powder consisting of innumerable microscopic crystals will undoubtedly scatter part of this light according to the laws of diffuse reflection, the remaining light being absorbed by the crystals. In principle one can determine the energy absorbed by the crystal by measuring the incident energy and all of the diffusely scattered light. However, the measurement of the luminescence emerging from the powder as a whole, and what is more important, the determination of the light emitted by the luminescent centers themselves, is extremely difficult. The reason for this is the permanent entrapment of part of the light produced in the crystal. This may be understood in the following way. Any light ray that strikes the surface of a medium, of index of refraction n , will be completely reflected if its angle of incidence is greater than the critical angle which is given by $\theta_0 = \text{arc sin } 1/n$. To illustrate, suppose that the crystal is perfectly spherical, then from simple geometry all reflections that an arbitrary

light ray in the interior of the crystal will make at the surface are at the same angle. Thus if this angle is greater than θ_c the ray will be permanently entrapped, until absorbed by the medium or escaping after being scattered, or suffering a reflection on an imperfection, that changes its angle of incidence. Gillette(13) has calculated that 70.0% of the luminescence formed in an optically perfect sphere of CdWO_4 is so trapped and that 73.0% is trapped in an optically perfect rectangular prism. Equivalent values for CaWO_4 are 56.2% for a sphere and 62.6% for the prism.

If one had a phosphor of perfect spheres, rectangles, or other calculable shapes, in principle the amount of light measured outside of such a material could be related to that emitted internally by the luminescent process. The fact that the perfect particles would be randomly oriented could probably be treated in a manner similar to that described by Longini(14) for sheets of particles. Also, the fraction of light escaping from randomly shaped crystals has been calculated. To accurately relate the light escaping from actual powdered crystals to that formed in their interior seems to be extremely difficult, if not impossible, for the following reason. Powders of a crystal are neither perfect geometric shapes nor completely randomly shaped. They are very imperfect microscopic images of their macroscopic habit, e.g., powdered rock salt, NaCl , consists of small nearly cube-like bodies with smaller various size cubes "knocked" off of their corners. To calculate the amount of light escaping from such quasi regularly, or perhaps quasi randomly, shaped crystals seems formidable indeed.

Obviously, for an accurate efficiency measurement with powders this problem must be solved. An experimental approach has been taken by

Betden and Kröger(15) who try to correct for these difficulties by calibrating their apparatus in such a way that the entrappment of light is compensated for. They estimate that efficiency measurements made in this way are accurate to $\approx 5\%$.

B. Efficiency Measurements with Slabs of Luminescent Materials

In contrast with efficiency measurements on crystalline powders discussed above we now consider the problem of making an efficiency measurement on a large single crystal. Most often we can obtain such materials as rectangular parallelepipeds, which for computational purposes may be regarded as slabs.

The amount of energy imparted to a slab may be easily determined particularly if its surface has good optical qualities, i.e., is reasonably flat and free from scratches. From such a surface one may measure the reflection with high precision and assume that for any beam incident on the crystal the energy not reflected is totally absorbed. Note that one may conveniently measure the reflections from a material even though it is completely opaque to the light being used.

The light incident on a crystal that is not reflected is, of course, refracted at the surface. Should the material be highly absorbent, all of the absorption will take place in the layers just adjacent to the surface. Thus, if a ray of ultraviolet excited luminescence in such a crystal one can assume, to a high degree of precision, that the excited centers are located just below the surface at the point the ray entered it. This may seem to be a trivial point but CaWO_4 and CdWO_4 so strongly absorb 2537 Å light that it is probably impossible to determine the index of refraction at this wavelength and thus in principle one cannot determine

the path of the refracted beam given the locus of the incident beam. This point will become clearer when we consider the emission for CaWO_4 and CdWO_4 in detail.

If the exciting light is weakly absorbed by the crystal it will cause luminescence to be emitted along the path of the refracted ray. For such a material it would be necessary to know both the index of refraction and absorption coefficient of the exciting ultraviolet in order that the distribution of excited centers, along the path of the exciting light, can be calculated.

We have just given the details of the process whereby energy is imparted to the luminescent centers in a slab of material. We now want to calculate the intensity of luminescent light, outside of the slab, emitted by these centers in the interior. For this purpose assume that light is emitted isotropically from a point in the slab. Here, perhaps, a digression is necessary since no experimental evidence exists showing that isotropic emission is the actual case. Such evidence would be difficult to obtain with powders since they would be randomly oriented if a large number were involved. However, if luminescence is not emitted isotropically this could conceivably be demonstrated with large crystals.

Let the arbitrary point, from which the light is emitted, be the point labeled s in Fig. 3. Light striking the surface at an angle θ less than the critical angle θ_c will be reflected or refracted as we have already considered. Let us inquire about the fate of the light outside of the cone of transmission where there is total reflection. By multiple reflections it will go to the ends of the slab where it will either pass

out of the slab or by making several reflections proceed towards the opposite end. One can show that for an optically perfect rectangular parallelepiped, which is perfectly transparent, and for which $n < \sqrt{2}$ all of the totally reflected light will ultimately pass out of the crystal through the ends of the slab. Since all of the crystals of interest to us have $n > \sqrt{2}$ we will not pursue this theorem further. For CaWO_4 and CdWO_4 the permanently entrapped light must meet with one of two fates, either it will be absorbed in the crystal in which case we do not have to consider it further, or it will meet with an optical imperfection, e.g., a scratch on the surface, which will allow it to escape from the crystal. In the latter case it may be detected along with the light which we wish to measure, necessitating that we make a correction for this additional scattered light.

The light that strikes the surface with $\theta < \theta_c$ will pass out of the crystal or be reflected. However, if it is reflected from the front face it may pass out of the back surface. Again, at the back surface it can be reflected, possibly passing out of the front and so on. To begin with, consider only light that passes out of the front surface the first time it strikes it. Any ray will be refracted at the surface according to Snell's law,

$$n \sin \theta = \sin \phi \quad (2)$$

where $n = 1$ outside of the slab. All such incident and refracted rays will define planes which will also pass through the line SS' . When observed from outside of the crystal, rays that originate at S will appear to come not from S but from a virtual source(16). It is most convenient

for calculation to fold together along the axis SS' all of the planes containing incident and refracted rays thus making a two dimensional case out of the problem of determining the position of the virtual sources. Let d be the distance of the point S from the front of the slab then if α and β are the coordinates of the virtual source, α/d and β/d are dimensionless quantities given by

$$-\alpha/d = \frac{1}{n} \left\{ - (n^2 - 1) \tan^2 \theta + 1 \right\}^{3/2} \quad (3)$$

$$\beta/d = (n^2 - 1) \tan^3 \theta \quad (4)$$

For illustration, the coordinates of the virtual source, corresponding to the different values of θ , are plotted in Fig. 4 for CaWO_4 for red and blue light.

Returning to the actual three dimensional case we see that all of the light from S that is directed toward the front face of the slab between the angles θ and $\theta + d\theta$ can be regarded as originating along the circle which is the locus formed by rotating the virtual source around the line SS' . If I is the total luminescent flux originating from S then $\frac{1}{2} \sin \theta d\theta$ is the flux striking the surface in the cone between θ and $\theta + d\theta$. This flux may be looked upon as emanating from the virtual source in the cone between ρ and $\rho + d\rho$ and striking the screen in the area swept out between the ray ρ and the ray $\rho + d\rho$ as they are rotated about the line SS' . Let this area be dA_ρ and let r_ρ be the distance from the virtual source to the point where the "ray θ " strikes the screen, then

$$dA_{\rho} = \frac{r_{\rho} d\rho}{\cos \rho} \quad 2\pi (r_{\rho} \sin \rho + \beta)$$

Call L , the luminous flux, per unit area, striking the screen in the cone between ρ and $\rho + d\rho$, then

$$\begin{aligned} L(\rho, \beta) &= \frac{I}{2} \sin \theta \frac{d\theta}{dA_{\rho}} \\ &= \frac{I}{2} \frac{\sin \theta \cos \rho d\theta}{r_{\rho} d\rho \cdot 2\pi (r_{\rho} \sin \rho + \beta)} \end{aligned}$$

From $n \sin \theta = \sin \rho$

$$\sin \theta d\theta = \frac{\cos \rho \sin \rho d\rho}{n \sqrt{n^2 - \sin^2 \rho}}$$

therefore,

$$L(\rho, \beta) = \frac{I \cos^2 \rho \sin \rho}{4\pi r_{\rho} n \sqrt{n^2 - \sin^2 \rho} (r_{\rho} \sin \rho + \beta)} \quad (5)$$

It is important to notice that in deriving this formula we have not taken into consideration the fact that some of the light is reflected at the surface. To include this we have only to include a factor $(1 - R_{\rho})$ where R_{ρ} is the fraction of light reflected at angle ρ . The expressions for R_{ρ} are well known(11,12).

We will use, in our computations, the special case of (5) obtained when d approaches zero. Physically this corresponds to the case of luminescence being formed just beneath the crystal surface. Allowing d to

go to zero (5) becomes

$$L(\phi, D) = \frac{I \cos^4 \phi}{4\pi D^2 n \sqrt{n^2 - \sin^2 \phi}}$$

If, in addition, we allow ϕ to approach zero we have

$$L(0, D) = \frac{I}{4\pi D^2 n^2}$$

and then if we let n approach unity this expression becomes $I/4\pi D^2$, just as we would expect.

Likewise, if in $L(\phi, D)$ we put n equal to unity we again get the expected expression

$$\frac{I}{4\pi} \frac{\cos^2 \phi}{D^2} \cos \phi = \frac{I}{4\pi r_\phi^2} \cos \phi$$

To the intensity representing light going directly from the source point S must be added the components reflected from one or more surfaces. Of the light originally heading toward the back surface of the slab, a fraction R_ϕ will be reflected toward the front surface where the fraction $(1 - R_\phi)R_\phi$ will emerge to strike the screen. If the slab has thickness t this particular reflection component can be regarded as coming from a source a distance $2t + d$ from the front surface. (See lower left corner of Fig. 4). Likewise, the next most intense component first strikes the front surface then the back surface and finally passes out of the front surface which gives rise to the reflection factors $R_\phi^2 (1 - R_\phi)$. This component can be regarded as emanating from a source a distance $2t + d$

from the front face. The next component has reflection terms $R_\rho^3(1 - R_\rho)$ and a point of origin term $4t - d$, and the next terms are $R_\rho^4(1 - R_\rho)$ and $4t + d$, etc. For CaWO_4 the reflection fraction R_ρ is approximately 10^{-1} thus terms containing R_ρ^3 contribute less than a tenth percent. The total luminescent intensity at the point on the screen D, D' is given by

$$\begin{aligned} \Lambda(0,0) = \frac{I}{4\pi} \left\{ \frac{(1-R_{\phi_1}) \cos^2 \phi_1 \sin \phi_1}{r_{\phi_1, d} \sqrt{m^2 - \sin^2 \phi_1} (r_{\phi_1, d} \sin \phi_1 + \beta_1)} + \right. \\ \frac{(1-R_{\phi_2}) R_{\phi_2} \cos^2 \phi_2 \sin \phi_2}{r_{\phi_2, 2t-d} \sqrt{m^2 - \sin^2 \phi_2} (r_{\phi_2, 2t-d} \sin \phi_2 + \beta_2)} + \\ \frac{(1-R_{\phi_3}) R_{\phi_2}^2 \cos^2 \phi_3 \sin \phi_3}{r_{\phi_3, 2t+d} \sqrt{m^2 - \sin^2 \phi_3} (r_{\phi_3, 2t+d} \sin \phi_3 + \beta_3)} + \\ \frac{(1-R_{\phi_4}) R_{\phi_4}^3 \cos^2 \phi_4 \sin \phi_4}{r_{\phi_4, 4t-d} \sqrt{m^2 - \sin^2 \phi_4} (r_{\phi_4, 4t-d} \sin \phi_4 + \beta_4)} + \\ \left. \frac{(1-R_{\phi_5}) R_{\phi_5}^4 \cos^2 \phi_5 \sin \phi_5}{r_{\phi_5, 4t+d} \sqrt{m^2 - \sin^2 \phi_5} (r_{\phi_5, 4t+d} \sin \phi_5 + \beta_5)} + \dots \right\} \quad (6) \end{aligned}$$

At first it might seem that there is no difference between, e.g., ϕ_3 and ϕ_4 . The difference is that since these components come from different virtual sources the rays that strike the point D,D' are not inclined to the line SS' at the same angle. For practical purposes we will use this formula with $d = 0$ so that it reduces to

$$\begin{aligned} \mathcal{L}(D,D')_{d=0} = & \frac{I}{4\pi} \left\{ \frac{(1-R_{\phi_1}) \cos^2 \phi_1}{r_{\phi_1,0}^2 m \sqrt{m^2 - \sin^2 \phi_1}} + \right. \\ & \frac{(1+R_{\phi_2})(1-R_{\phi_2}) R_{\phi_2} \cos^2 \phi_2 \sin \phi_2}{r_{\phi_2,2\pm} m \sqrt{m^2 - \sin^2 \phi_2} (r_{\phi_2,2\pm} \sin \phi_2 + \beta_2)} + \\ & \left. \frac{(1+R_{\phi_4})(1-R_{\phi_4}) R_{\phi_4}^2 \cos^2 \phi_4 \sin \phi_4}{r_{\phi_4,4\pm} m \sqrt{m^2 - \sin^2 \phi_4} (r_{\phi_4,4\pm} \sin \phi_4 + \beta_4)} + \dots \right\} \end{aligned} \quad (7)$$

For computational purposes one does not try to find the ϕ_2, ϕ_4 , etc., that corresponds to rays that strike the point D,D' but computes each term for arbitrary values of these angles, makes a graph of $\mathcal{L}(D,D')$ as a function of D' and adds the values of the intensities of each component at the point D'.

The first three terms of Equation (7) and their sum are shown in Fig. 5 for parameters actually used in the CaWO₄ measurements.

The intensity I is put equal to one so that the ordinate is the fraction of emitted luminescence that strikes a unit area, on the photo cell, at the point D, D' .

One can write (7) for the case where θ , or the various ρ 's, is zero. This is the case that involves only rays close to the axis SS' . Physically it is applicable for a detector on the line SS' whose linear dimensions are small compared to the distance D . In this case (7) becomes

$$L(D,0)_{\theta=0} = \frac{I}{4\pi} (1-R_0) \left\{ \frac{1}{(\pi D)^2} + \frac{R_0(1+R_0)}{(\pi D + 2t)^2} + \frac{R_0(1+R_0)}{(\pi D + 4t)^2} + \dots \right\} \quad (8)$$

where R_0 is the value of R_ρ at $\rho = 0$. This formula is very useful for quick computations.

To summarize, we have calculated the intensity of luminescent light, emitted from a luminescent center in the interior of a slab of material, incident on a screen (detecting device) in front of and parallel to the face of the slab. Actually we will use this expression to calculate the emitted intensity from the intensity observed by a photocell. We do not fulfill completely the point source condition, but in the calibration procedure used some, if not all, of the error produced by the small extent of the source is compensated for.

The index of refraction n , which appears in all of these formulas, is a function of wavelength. The effect of this is that the distribution of luminescence outside of the crystal is different from that inside, that is, the observed spectrum is slightly different from that emitted by the luminescent centers. Once we have determined the luminescent spectrum

of these crystals we can compute the true spectrum from it.

IV. EXPERIMENTAL EQUIPMENT AND TECHNIQUES

For each crystal of CaWO_4 and CdWO_4 we will need the following information to measure the energy conversion from which we can calculate the quantum efficiency.

- a) The percent reflection of 2537 Å ultraviolet, particularly at the angles we will use for the efficiency measurements.
- b) The optical absorption of the materials, especially at 2537 Å, but also at the wavelengths contained in the emission spectrum.
- c) The indices of refraction at the wavelengths of the emission spectrum.
- d) The spectral distribution of the emission spectrum.
- e) An efficiency measurement, i.e., a determination of the amount of luminescence emitted when a known amount of energy is absorbed in the crystal.
- f) If all of the above measurements are at one temperature, a measurement of the temperature dependence of the efficiency is not necessary. However, ratios of the emission at room temperature, dry ice, and liquid air temperatures were obtained to compare with powder data on the temperature dependence of the efficiency.

A. Description of Equipment Used to Determine the Spectral Distribution

All of the spectrum determinations were made with a medium Hilger quartz spectrometer. The method that was used employed this spectrometer and its associated optics to obtain a spectrum of the luminescence on a photographic plate. Then, without disturbing this equipment the crystal

producing the luminescence was removed and an incandescent lamp of known emission was substituted for the crystal. In this way the spectrum obtained from the phosphor is compared to a known spectrum and such things as the resolution, transmission of the spectrometer, spectral response of the recording photographic plate, etc., are then "cancelled out."

With the aid of Fig. 6, which is largely self-explanatory, we will consider the details of this arrangement. All of the emission spectra were obtained with the crystal excited by 2537 Å ultraviolet. The light source was a G. E. Uviarc UV-2 quartz low pressure Hg discharge lamp operated from an autotransformer supplied by the manufacturer. In order to reduce the amount of ultraviolet that escaped into the laboratory the lamp was fitted with a housing containing a small exit port. The entire unit was then cooled with a small blower. By adjusting the amount of air admitted to the blower the steady state operating temperature could be closely controlled. After a one hour warm-up the output of the lamp was constant to within one or two percent over a period of two hours. If the room temperature changed markedly the lamp output also changed, sometimes to the extent that a run had to be discarded.

The light from the lamp was focused on the entrance slit of a small Hilger single monochromator with a quartz lens of approximately the same focal length as the collimating lens of the monochromator to obtain maximum light output. The monochromator was adjusted for optimum transmission of 2537 Å light which was focused on the crystal being studied with another matched quartz lens. Originally, considerable light from the more prominent Hg lines also emanated from the exit slit. Before this could be eliminated it was necessary to line the interior of all parts

of this instrument with black matte paper and install several additional baffles to eliminate spurious light scattering. In addition, it was necessary to place a filter between the lamp and the entrance slit that eliminated all of the unwanted lines but the 3650 Å one, which by tilting the crystal as described below, was reduced to a degree that it did not interfere with any of the measurements. On all of the emission spectra this line, and only this line, appeared faintly superimposed on the spectrum. With these modifications the intensity of light greater than 3000 Å striking the crystal being studied was less than 0.1% of that contained in the 2537 Å line.

The cryostat which was used to maintain the crystals being studied at a fixed temperature is shown in Fig. 8. Note that the crystal was inclined to the incident ultraviolet at 35° , and the spectrum observed at 10° , to the normal. This arrangement prevented the 3650 Å light from being reflected directly into the spectrograph. This occurs in the following way. 3650 Å light incident on the crystal was refracted along the normal of the crystal and partially reflected from its back surface directly into the spectrometer. In spite of this arrangement, a very small amount of 3650 Å light was still scattered into the spectrometer.

The crystal being studied was thermally connected with the copper block by embedding it in Wood's metal. In practice the crystal chamber was filled with molten Wood's metal. The crystal was then placed on the surface of the metal and the top plate of the block laid on it. With all parts slightly above the melting point of the Wood's metal, the top plate was screwed down, the excess metal spewing out of the small slit in the plate. When the top was firmly fastened and the metal had hard-

ened, any excess metal was removed with a tweezer. Several times it was possible to take off the lid of the crystal chamber without melting the Wood's metal. In every case, the metal completely filled the cracks between the crystal and the copper block.

The temperature of the crystal being studied was not determined directly, however, the temperature of the front surface of the block containing the crystal was measured with a copper-constantan thermocouple. Several months effort was expended in an attempt to measure the temperature of the exposed surface of the crystal, especially for measurements at liquid air and dry ice temperatures. These attempts were unsuccessful primarily because no good way could be found to fasten a thermocouple to the crystal surface that would provide sufficient thermal contact to really indicate what the crystal surface temperature was. For example, thermocouples, of two mil wire were soldered to 2 mm. by 2 mm. copper foil, 0.2 mil thick, and these in turn were fastened directly to a copper block, at liquid air temperature, with a very thin layer of glyptal. The temperature indicated by this couple was from 25 °K to 50 °K, depending on the thickness of the glyptal layer, higher than similar thermocouples soldered directly to the same block. Thermocouples placed in holes in the crystals themselves always read the same as those on the copper block. Since CaWO_4 and CdWO_4 are fairly dense crystalline substances one expects that they have good enough thermal conductivity so that the crystal surfaces are only slightly above the temperature of their interior. There is no direct experimental evidence to support either of these suppositions. The procedure followed when making a run was to pump the vacuum chamber of the cryostat down to 10^{-6} mm. Hg. or

better, then fill the coolant chamber with dry ice, liquid air, or water for room temperature measurements, and allow at least 30 minutes for the crystal to reach equilibrium, even though the copper block reached the coolant temperature almost immediately.

That the incident ultraviolet light could not have raised the temperature of the crystal more than 0.1°K is shown by the fact that when this same amount of ultraviolet was focused on the vacuum radiation thermocouple, to be described below, which certainly had considerably less heat capacity, its temperature changed by only 0.1°K .

Accurately timed spectrograph exposures were made at liquid air, dry ice, and room temperature after the thirty minute waiting period for each coolant. Except for the difficulty involving the surface temperature mentioned above, the crystals were at $78 \pm 2^{\circ}\text{K}$ when at liquid air and $195 \pm 3^{\circ}\text{K}$ when at dry ice temperature. Because it proved difficult to keep the dry ice acetone mixture, or powdered dry ice which was sometimes used, well stirred, runs with this coolant suffered from larger fluctuations than when liquid air was used. Also, if the mixture was stirred too vigorously it supercooled. Following these measurements the cryostat was removed and a G. E. standard pyrometer lamp was substituted for the crystal. This arrangement is described by Fig. 7. The lamp consisted of a flat tungsten filament notched at the point where, in the center of the filament, the color temperature was known. Both the lamp and the crystal could be very accurately located at the same point by using a simple trick. An incandescent lamp was located where the cassette for the photographic plate normally fitted (at the visible end of the spectrum). This produced an image of the entrance slit of the spectrom-

eter, as formed by the achromat, at precisely the spot where they should be located. Locating the image on the proper spot of the lamp or cryostat was accomplished easily by means of adjustment screws that allowed them to be moved horizontally or vertically.

Thus the spectrometer, the associated optics, and the photographic plate were not disturbed during an entire run, only two different light sources were used. In this way the spectra and a series of exposures of known intensity were obtained on the same photographic plate, an Eastman type II. Thus the transmission of the spectrometer, of the lenses, and also the spectral response and the development conditions of the photographic plates, etc., were the same for all exposures.

The lamp manufacturer supplied its brightness temperature, at the indicated point on the filament, for a current of 30.00 amperes, and the transmission of the glass envelope. From this data and the emissivity of tungsten, as given by Forsythe and Adams(17), the spectral distribution of the light emitted by the filament was calculated. The emission of partially black bodies such as this are treated in detail by Forsythe(18). The spectral distribution of the calibrating lamp is shown in Fig. 9.

Because the lamp was on the order of 10^6 times brighter than the crystal emission it was necessary to impose a sector wheel between the lamp and the spectrometer. The transmission of this wheel was about 3×10^{-7} . This small value was obtained by placing two pairs of slits on opposite edges of a disk. The separation of the slits could be accurately adjusted by putting a steel foil between them and then removing the foil after the slits were securely screwed down. The disk was rotated

at 1750 rpm.

The pyrometer lamp was operated from the direct current mains with a battery floating across it. The current was measured with a type K potentiometer. Except where large surges affected the mains, the current could be kept within 0.01 percent with constant monitoring. Since most of the data was taken at night, no surges long enough to cause a run to be discarded occurred after daytime operation was abandoned.

When calibrating the plate, exposures of 0.02, 0.04, 0.08, . . . , 10.24 minutes were made. This method was adopted when preliminary measurements indicated that there was no reciprocity failure in the useful blackening range. Unfortunately, when the data had been completed and the plates carefully densitometered, it was found that they did not completely obey the reciprocity law, $D = I_0 t$, where D is the density, I_0 the intensity, and t the time, but did obey the Schwarzschild relation(19), $D = I_0 t^p$, where p is supposed to be a constant for a given emulsion and development. Actually, the values obtained for p were very close to unity and constant so that the reciprocity failure was not great. However, the plates were analyzed using the Schwarzschild relation by the method given below.

Besides the ten calibrating exposures and the nine luminescent spectra a wavelength scale was photographed on each plate. Incidentally, it had been checked against an iron exposure and found to be extremely accurate. When densitometering the plates, the filament image was turned parallel to the markers on the wavelength scale and the plate then scanned, at a fixed wavelength, across all of the exposures. An example of these densitometer tracings is contained in Fig. 11. Then for each wavelength

one can compare the density of the luminescent spectra to the density obtained from the calibration curve. The process used was to plot $\log D$ against $\log t$ for the calibrating exposure as well as the luminescent exposures. Note that the Schwartzchild relation can be written

$$\log D = \log I + p \log t$$

for the spectrum exposures, and

$$\log D_0 = \log I_0 + p \log t$$

for the calibration exposures. Then for any time t

$$I = I_0 D / D_0$$

which is just the ratio's of the ordinates of the two plotted lines. In Fig. 12 we show the curves obtained at 4250 Å for one of the CaWO_4 spectra.

B. Description of Apparatus Used for Efficiency Measurements

To make an efficiency measurement one must determine the fraction of energy imparted to a crystal that emerges as luminescent light. To this end one must be able to measure the incident energy, which in practice is focused on a small area 0.2 mm x 2.0 mm, and also the emitted light which diverges according to the inverse square law from this point as well as being reduced approximately by the factor $1/n^2$ (see Eq. 8). The energy available for the latter measurement is about 10^{-3} that of the former. One does not need to know these energies absolutely; it is sufficient to know only their ratios. For this reason and to put all measurements on a common basis, the incident energy is measured with a black radiation thermocouple and the photocell used to detect the luminescence was cali-

brated in terms of the same thermocouple.

The phototube used for all measurements was a R.C.A. type 935 blue sensitive tube. The associated circuit, shown in Fig. 13, is based on a circuit given by Victoreen(20). An important aspect of this circuit is the arrangement whereby the input resistances R_1 , R_2 , R_3 , R_4 , can be quickly changed. In order to determine if the sensitivity, i.e., if the galvanometer deflection, was directly proportional to the input resistance, the following test was done with resistances of 5×10^5 , 10^6 , 5×10^6 , and 10^7 ohms. A diaphragm with two openings was placed in front of the phototube and the intensity of an incandescent lamp, some distance from the diaphragm, adjusted so that near full scale deflection was obtained with one of the holes open and the other closed. Readings were then taken with each hole open separately and then with both open but using a smaller input resistor. In this way the linearity of the circuit using these input resistances was established. When using the photocell for measurements the input resistances were chosen so that nearly full-scale deflections were always obtained. One percent wire wound or glass enclosed Victoreen resistors were used. This introduces an error of approximately two percent in all of the measurements with the photocell that involves changing the input resistors.

In practice, the zero drift is the next most important factor that limits the accuracy of this circuit. Because of this, measurements were always taken in the following way. The zero was first adjusted, the light to be measured admitted to the tube by opening a shutter, the deflection noted, the shutter closed, the zero reading noted and then, if

it was necessary, the deflection was corrected for a shift in the zero reading.

The radiation thermocouple was constructed by H. Cartwright and is similar to the one described in Chapter VIII of Strong(21). This particular thermocouple contained two single junction couples connected to provide compensation for changes in the ambient temperature. Its vacuum chamber was connected to a large charcoal trap which was heated to 440°C, to activate the charcoal, whenever the chamber was evacuated. After the initial evacuation, which required 9 hours, a pressure of 5×10^{-7} mm was reached. Although the thermocouple was pumped down to this pressure several times there was no indication that while measurements were in progress the pressure had ever risen to a point where the thermocouple sensitivity was affected.

The thermocouple was used with a Liston-Fold chopper amplifier that drove a secondary standard type large scale milliammeter. The gain of this amplifier changed from day to day according to the vagaries of the mechanical chopper. Thus, in order to use this amplifier very frequent calibration was required. This was done using the "built in" test signal. The absolute value of the test signal was not used, only its constancy during a given run and this was often checked by measuring the voltage of the test signal battery which varied less than one-half percent during all runs.

In order to calibrate the photocell in terms of the radiation thermocouple the optical system diagramed in Fig. 14 was built. The light, of any of the prominent Hg lines, emitted by the monochromator was made parallel by an achromatic lens. By means of the two position mirror this

light was directed either toward the photocell or the thermocouple. A diaphragm exactly the same size as the opening to the photocell was arranged, as is shown in the diagram, so that equal amounts (the same solid angles are subtended) of light strike the photocell and the thermocouple. To calibrate the photocell the output of the monochromator was adjusted to the desired thermocouple reading, then the mirror was rotated so that the light struck the photocell and its response noted. This procedure was repeated numerous times for each of the Hg lines. The spectral response curve for the photocell so obtained is shown in Fig. 15. The ordinate is given as $\text{mm}/\mu\text{v}$ but this is only for convenience as the micro-volt scale is relative, not absolute.

By adjusting the height and width of the exit slit of the monochromator the image formed by the paired achromats was very nearly the size of the "spot" of luminescence on the crystals studied. To a large extent this compensates for making calculations using the approximations that the luminescence originated from a point source. This is particularly so since the solid angle subtended by the photocell when being calibrated was the same as when it was used for efficiency measurements.

Figure 16 is a schematic drawing of the way the apparatus was used for the efficiency measurements. Since only 2537 Å ultraviolet is needed the monochromator and light source were applied in the same way they had been for the spectrum measurements. The two position mirror was again used to focus light alternately from the thermocouple to the crystal being studied. Inasmuch as 2537 Å light is not visible and since the optics were quartz and not achromatic it proved to be difficult to focus the 2537 line on the thermocouple. This was not satisfactorily accomplished

until the thermocouple and a luminescent uranium glass plate located in the same plane as the thermocouple collector were mounted on a microscope stage. Then the ultraviolet was focused on the glass and the stage moved laterally until the thermocouple reading indicated that the image was entirely on the collector. Incidentally, the image is much smaller than the collector. The stage controls are so sensitive that the image could be properly located with only reasonable care.

Focusing the beam on the crystals was easy because they were, of course, luminescent. The accurate location of the photocell with respect to the crystal, or the image on the photocell side of the calibration setup, could be easily done with a simple jig. The crystal was mounted on a stand that held a slide containing openings of different sizes. These openings symmetrically surrounded the image, or luminescent spot, and expose a series of different areas of the crystal. However, none were so small as to interfere with the primary "spot" of luminescence. When the luminescence was measured using the largest and smallest openings, and with the incident ultraviolet held constant, there was only 1 or 2%, depending on the crystal used, difference between the readings. This shows that very little of the entrapped light escapes, or at least contributes enough to the components we wish to measure, to introduce an error larger than this amount.

Once the components were properly adjusted, the efficiency measurements consisted simply of alternating the 2537 Å between the thermocouple which measured the incident energy and the crystal being studied. Photocell readings were taken for different intensities of ultraviolet and in

this way the linear dependence of the luminescence on the incident energy was established.

C. The Reflection and Transmission Equipment

The reflection measurements were made by standard methods, however, Fig. 17 is included for completeness. One point that should be mentioned is that there was an uncertainty of between one-half and one degree in the angle of incidence due to lack of reproducibility in mounting the CdWO_4 crystals because of slight unevenness around their edges. Another difficulty with CdWO_4 will be considered when we discuss the results of the reflection measurements.

A Beckman model DU quartz optic spectrophotometer was used for the transmission measurements. In all cases the transmission was measured relative to the air path in an equivalent beam. When attempting to measure the transmission at wavelengths where the light could excite luminescence, the photocell detected this light. In order to correct for this a filter that was completely opaque to the ultraviolet was interposed between the crystal and the detector. Then at any given wavelength, in the region where the filter is opaque, the actual transmission is zero and the detector response is entirely due to luminescent light. The reading with the filter, corrected for the fact that the filter is not 100% transparent, can then be subtracted from the reading obtained with the detector responding to both transmitted and luminescent light.

V. MEASUREMENTS ON CaWO_4 AND CdWO_4

In all, the efficiency measurements described here apply to two crystals of CaWO_4 and two of CdWO_4 . All four were obtained from the Linde Air Products Laboratory at Tonawanda, N. Y. The CaWO_4 crystals were both 1.0 mm. thick, crystal #1 was 6 mm. by 10 mm. and crystal #2, 6 mm. by 8 mm. Both had their "C" axis parallel to their long dimension. Unfortunately, the crystals were differently oriented with respect to the "a" axis. CaWO_4 is slightly birefringent(22) ($n = 1.9105$ and $n = 1.9260$ at 6907 Å) so that one can regard the material as isotropic and use the average index of refraction. Had the accuracy of the measurements warranted it the crystals could have been oriented by X-ray methods and accurate indices used for calculation. One can see from Eq. (8) that the error in the energy conversion, due to uncertainty in the index of refraction, is approximately the square of the error in the index of refraction. Except for the possibility that the index varies from piece to piece, the uncertainties in the values given by Harada(22) for CaWO_4 , which were used throughout, are negligible compared to the other errors in the efficiency measurements.

The two crystals of CdWO_4 , were cleaved with their surfaces perpendicular to the "c" axis but not otherwise oriented. The edges of crystal #2 were ground perpendicular to the largest surface and slightly polished. Because of the tendency of this material to cleave, the edges frayed slightly and no further polishing was attempted. This crystal was 6 mm. by 10 mm. and 0.75 mm. thick. It was transparent though colored pale yellow. The coloring was slightly uneven. Because of

the difficulties encountered with CdWO_4 crystal #2, shaping the other one was not attempted. It was 0.90 mm. thick and approximately 15 mm. by 10 mm. and had rough edges that were somewhat discolored. This discoloring extended into one end of the crystal in bands of approximately 2 mm. wide. The unevenness of coloring in both crystals can probably be attributed to the presence of an impurity or an excess of one of the constituents, perhaps Cd. Unfortunately, accurate indices of refraction for CdWO_4 are not available. Gillette(13) gives 2.4, a value which seems to be too high. We will describe below the attempts to determine the index of refraction for CdWO_4 from transmission measurements.

A. The Reflection Measurements at 2537 A

1.) CaWO_4 . The reflection of 2537 A light from both CaWO_4 crystals is indicated by Fig. 18. The fact that #1 reflected two percent more than #2, which is 20% reflectionwise, can perhaps be explained in the same way that the differences discussed below for CdWO_4 can be explained. However, the measurements were always reproducible for each of the crystals and for different regions on the same crystal. The measured reflections were used and thus this difference does not introduce an additional error in the efficiency measurements.

2.) CdWO_4 . Initially it proved to be difficult to obtain reproducible reflection data for the CdWO_4 crystals. The error in the reflection measurements is about 0.5%. Originally, the spread in the reflection data was greater than 2%. In Fig. 19 a large number of reflection measurements are plotted indicating the spread found. Now the beam of ultraviolet used for these measurements is very nearly the size of the luminescent "spot" for which the efficiency measurements apply. The

circled points, connected by the dotted lines, indicate why the reproducibility is poor. The points at 10° , 20° , and 30° were made at one spot on the crystal and the other circled points at an adjacent spot with all other parameters held constant. This indicates that the reflection of this material is not uniform over the surface of the crystal. The theory of reflections from insulators predicts that the reflection coefficient should be higher in regions containing impurities than in pure regions. To minimize this difficulty, the reflection measurements actually used were made at the same spot on the crystal that was used for the efficiency measurements. They are plotted in Fig. 20.

B. The Transmission Measurements

1.) CaWO_4 . The transmission of both crystals for wavelengths of 2200 Å to 7000 Å is shown in Fig. 21. This shows clearly that there is no serious absorption in the region of the emission spectrum. The region of the cutoff is expanded in Fig. 22 which shows that crystal #2 is slightly more absorbing than #1. This is in agreement with the observation that this crystal is more reflecting than the other. Figure 23 demonstrates that for crystal #2 all of the photocell response for wavelengths below 2700 Å is due to the luminescence excited by the light in the beam of the spectrophotometer. The method used to demonstrate this was discussed in the section on experimental methods. Similar data for crystal #1, Fig. 24, is not so clear but the same interpretation can be made. The errors at such small transmissions are large enough so that all of the observed response can still be attributed to luminescence.

The measurements indicate that if thin enough samples were available there might be some transmission at 2537 Å. In as much as the absorption of 2537 Å could not be determined one could not determine the distribution of luminescence along the path of the exciting ultraviolet. Since one would like to make the assumption that all of the observed luminescence originated directly below the surface of the crystal the following experiment was performed. A beam of 2537 Å ultraviolet was focused on a very small area at the upper edge of all of the crystals. The luminescent spot was observed with a 20 power glass. The penetration of the ultraviolet into the crystal greater than 0.1 mm. should be easily observed with this arrangement. The observations indicate that the penetration must be less than this amount and thus the assumption that the luminescence originates very close to the surface of the crystal is justified. The same test was made with the CdWO_4 samples.

2.) CdWO_4 . - Transmission data for five different CdWO_4 crystals are plotted in Fig. 25. These crystals are completely opaque below 3100 Å. From 3150 Å to 4500 Å they show a thickness dependent absorption that is probably due to an impurity since even the thickest sample used was not completely opaque in this region. Since the emission spectrum extends from 4000 Å to 6000 Å, the observed spectrum is undoubtedly affected to some extent by this absorption. However, since better than 90% of the light observed in a spectrum determination penetrates only a very small thickness of the crystal, this must be a small effect. Crystal #4 was considerably less transparent than the rest and had a distinct cloudy appearance. No attempt was made to make any of the

other measurements with crystals of this type.

Again, the apparent transmission in the region of 2537 Å was shown to be due to the photocell detecting luminescence produced by the spectrophotometer light beam. Details of the measurements from 2000 to 3500 Å are shown in Fig. 26, and for the region 3000 to 6000 Å in Fig. 27.

It is well known that the transmission of a medium can be accurately calculated from the indices of refraction for light of wavelength that is much longer than the absorption edge. The measured transmission for CaWO_4 is in good agreement with that calculated from the refractive indices. Because the absorption edge of CdWO_4 is so close to the wavelengths contained in the emission spectrum it is questionable whether the transmission data can be used to obtain the indices of refraction of this material. Unfortunately, a more accurate value than the 2.4 given by Gillette(13) could not be found in the literature and it was necessary to resort to computing the index of refraction from transmission measurements. The uncertainties in this procedure is aggravated by the fact that one suspects this material is strongly birefringent. The procedure followed was to compute the index of refraction, n , for wavelengths in the entire transmission region, from the measured transmission assuming no absorption. Obviously, see Fig. 25, this assumption is incorrect where absorption is present, e.g., at 3700 Å.

When the calculated n 's were plotted against λ one could not determine by inspection the region where absorption was present. A more elaborate procedure was then tried which yielded seemingly good

values of n . Data from two widely separated λ 's, e.g. 5000 Å and 7000 Å, were used to compute the values of A and λ_s in Sellmeier's Equation

$$n^2 = 1 + \frac{A^2}{\lambda^2 - \lambda_s^2}$$

Different pairs of λ 's were tried until it was found that for all λ 's above 5500 Å the same A and λ_s applied. These values, $A = 4.00$ and $\lambda_s = 2044$ Å, were then used to compute the indices needed for the calculation of the energy conversion. The energy conversions so obtained, discussed in detail below, are improbably high indicating that the indices yielded by this procedure are too large. This suggests that there is sufficient absorption throughout the entire region of the transmission measurements to invalidate this procedure. Because no better values are available there was no choice but to use these admittedly unreliable indices in calculating the luminescent data.

C. Luminescent Spectrum Measurements

The spectrum measurements on the two CaWO_4 crystals are shown in Figs. 28, 29, 30, and the CdWO_4 measurements in Figs. 31, 32, and 33. Some points which deviate markedly from the cluster of points can in all but a few cases be directly attributed to imperfections in the film. Even so the spread of the points is greater than the preliminary measurements, at room temperature, indicated that they should be. The most probable explanation for this is that these plates were developed under conditions where temperature control was extremely difficult. The averages of data from each crystal and each type of crystal are less than

the experimental error and thus the differences between different crystals are not significant. For comparison the spectrum measurements of Kroger(4b) are also shown with the liquid air measurements, Fig. 28. Note that his spectra were obtained with powders and not single crystals.

It is apparent from the dependence of the index n and reflection ratio R on wavelength that the observed spectra will be slightly different from that actually emitted by the luminescent centers in the interior of the crystals. The observed spectra from CaWO_4 and the spectra corrected to the interior are shown in Fig. 34. Both spectra are matched at the peak of the observed spectra. Obviously, the difference is slight so that we have used the observed spectra in computing the energy conversion at room temperature. In addition, the comparison of the temperature dependence of powders, also from Kroger(4c), with that which we obtained is given in Figs. 35 and 36. The efficiency at -180°C is taken as 100% for both crystals.

One may ask whether the spectra are the same at the different temperatures. For CdWO_4 the differences are less than the experimental error. Also, there is no clear difference between the CaWO_4 spectra observed at 77°K and 195°K . The room temperature result is slightly different from these other two as is indicated in Fig. 30 where both the 300°K and 195°K spectra are shown, after their scale was adjusted to match the 77°K curve. In all computations the spectral distributions we obtained were used.

D. The Efficiency Measurements

1.) CaWO_4 . - To within experimental error the luminescent light emitted by both crystals is a linear function of the exciting ultraviolet,

Fig. 37. Also, there is a marked difference between crystals. From the ratio of photocell deflection to thermocouple deflection the energy conversion and the quantum efficiency given in Table I were computed. Both were determined at room temperature. The error involved in a com-

Table I

Energy Conversion and Quantum Efficiency of CaWO_4

<u>Crystal</u>	<u>Energy Conversion</u>	<u>Quantum Efficiency</u>
CaWO_4 #1	.45 ₅	.74 ₇
CaWO_4 #2	.50 ₅	.82 ₈

parison of the efficiencies is smaller than the observed difference. This difference is supported qualitatively by the observation made during the spectrum determinations that one crystal always produced a darker spectra on the photographic plate than the other crystal for equal exposures.

Since it is difficult to ascribe these large differences to purely experimental errors it is conceivable that the thermal history of the two crystals is different enough so that an effect similar to one found by Kroger(24) for re-crystallized powders is also operating here. Also, the degree of polarization in the exciting radiations, if any, was not determined. Therefore if there is a connection between the degree of excitation and the direction of polarization, as yet unknown, the fact that the two samples were oriented differently would produce such a difference. This is just one of a number of questions suggested by this investigation.

One may compare the quantum efficiencies obtained here with the 0.71 given by Kroger(4d) for powdered CaWO_4 . Presumably his measurements were made with the equipment described by Botden and Kroger(15), though an explicit statement of this was not found in these papers. There is no mention of a correction being made for the permanent entrapment of some of the emitted luminescence, a subject previously considered in detail. This correction would increase the quantum efficiency given by Kroger by at least 10%. Thus the efficiencies attributed to powders and our two single crystals are in substantial agreement.

The error that should be attached to the efficiency measurements is uncertain since two possible sources of error were not evaluated explicitly. Namely, the validity of the assumption that the luminescent "spot" in the crystal can be treated as a point, and secondly, it was assumed that the spatial distribution of the light intensity in the cone of light used to calibrate the photocell was approximately that of the luminescence. This second possibility could introduce a large error only if the sensitivity of the photocell cathode was not uniform over its surface. Notwithstanding, the error in the CaWO_4 efficiency is probably not greater than 5%. With more elaborate equipment, and somewhat larger crystals, more precise measurements could easily be made.

2.) CdWO_4 . - Like the CaWO_4 the energy conversion of the two crystals of CdWO_4 differed more than the experimental error as shown in Fig. 37. It was expected that these crystals would be less alike since, as we described above, they differed in appearance. The quantum efficiencies and energy conversion given in Table II, were calculated from

the measurements using the index of refraction obtained from the transmission measurements.

Table II

Energy Conversion and Quantum Efficiency of CdWO_4

<u>Crystal</u>	<u>Energy Conversion</u>	<u>Quantum Efficiency</u>
CdWO_4 #1	.54 ₇	1.0 ₃
CdWO_4 #2	.65 ₁	1.2 ₂

The fact that the quantum efficiency is close to unity for both crystals raises a question as to the accuracy of the CdWO_4 measurements. At lower temperatures the quantum efficiencies are even higher, as indicated by Fig. 36. It is apparent that it is energetically possible for the efficiency to be greater than unity but if only one luminescent center is involved in the process it is difficult to conceive of how the single center may emit two quanta. However, if, in this material, there is energy transport from one center to another, see e.g. Botgen(23), then a quantum efficiency greater than unity is feasible.

A more likely explanation is that the index of refraction we have used is too large. This would result from impurity absorption in our material increasing the measured absorption which in turn would make the refractive index, calculated from the absorption, too large. The high efficiency could also result from this material being birefringent, which again, would mean that we have used an incorrect refractive index.

Future Work on CaWO_4 and CdWO_4

The room temperature results for CaWO_4 are probably reliable. How-

ever, the CdWO_4 results and the low temperature measurements are subject to question since several properties, which we will enumerate below, of these crystals are not known.

1.) - The refractive index and transmission of both materials should be investigated with emphasis on crystal to crystal variations and possible temperature dependence.

2.) - The reflection and absorption of 2537 Å light should be determined as a function of temperature. The lack of agreement of our measurements and the powder data shown in Figs. 35 and 36 can be explained if one or both of these quantities is temperature dependent.

3.) - The possibility that the energy conversion may in some way depend on polarization of the exciting ultraviolet and/or the direction of polarization with respect to the orientation of the crystal has not, to our knowledge, been investigated.

4.) - One should look for the effect of long high temperature thermal annealing which presumably would effect the perfectness of the lattice.

5.) - For both of these materials it was ascertained that only a negligible amount of light that normally would have been permanently entrapped in the crystal was scattered in the detector from parts of the crystals further than 1/2 mm. from the luminescent "spot." The possibility still exists that an appreciable amount of scattering of this entrapped light occurred closer to the "spot."

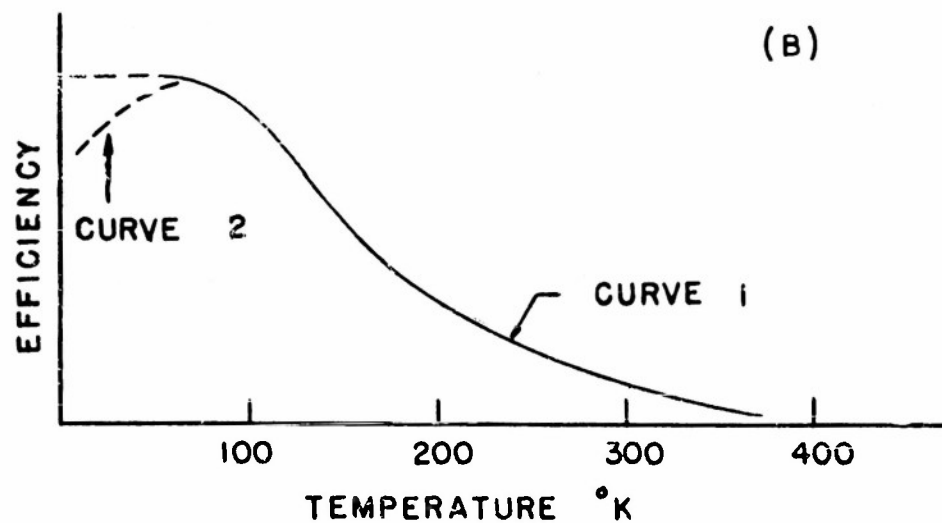
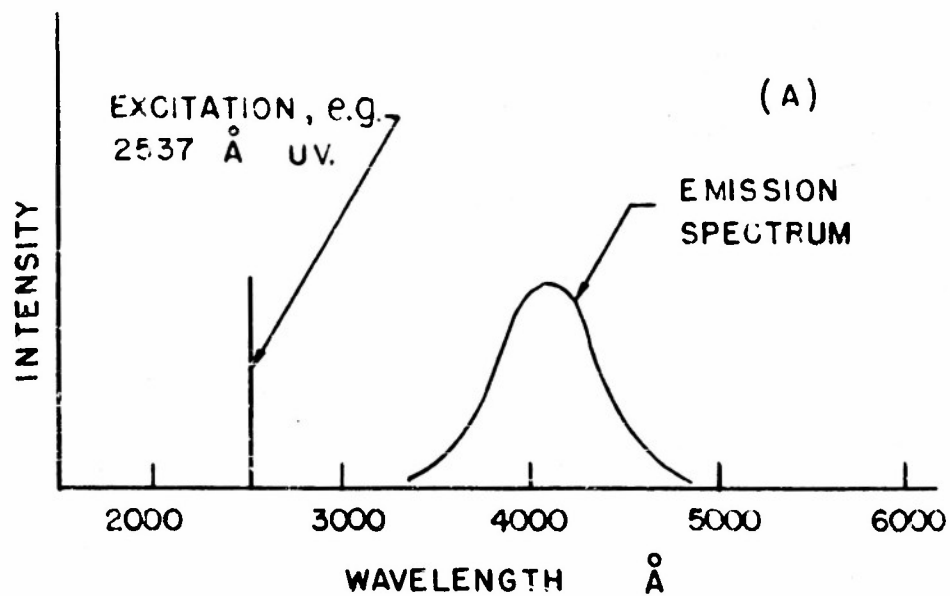
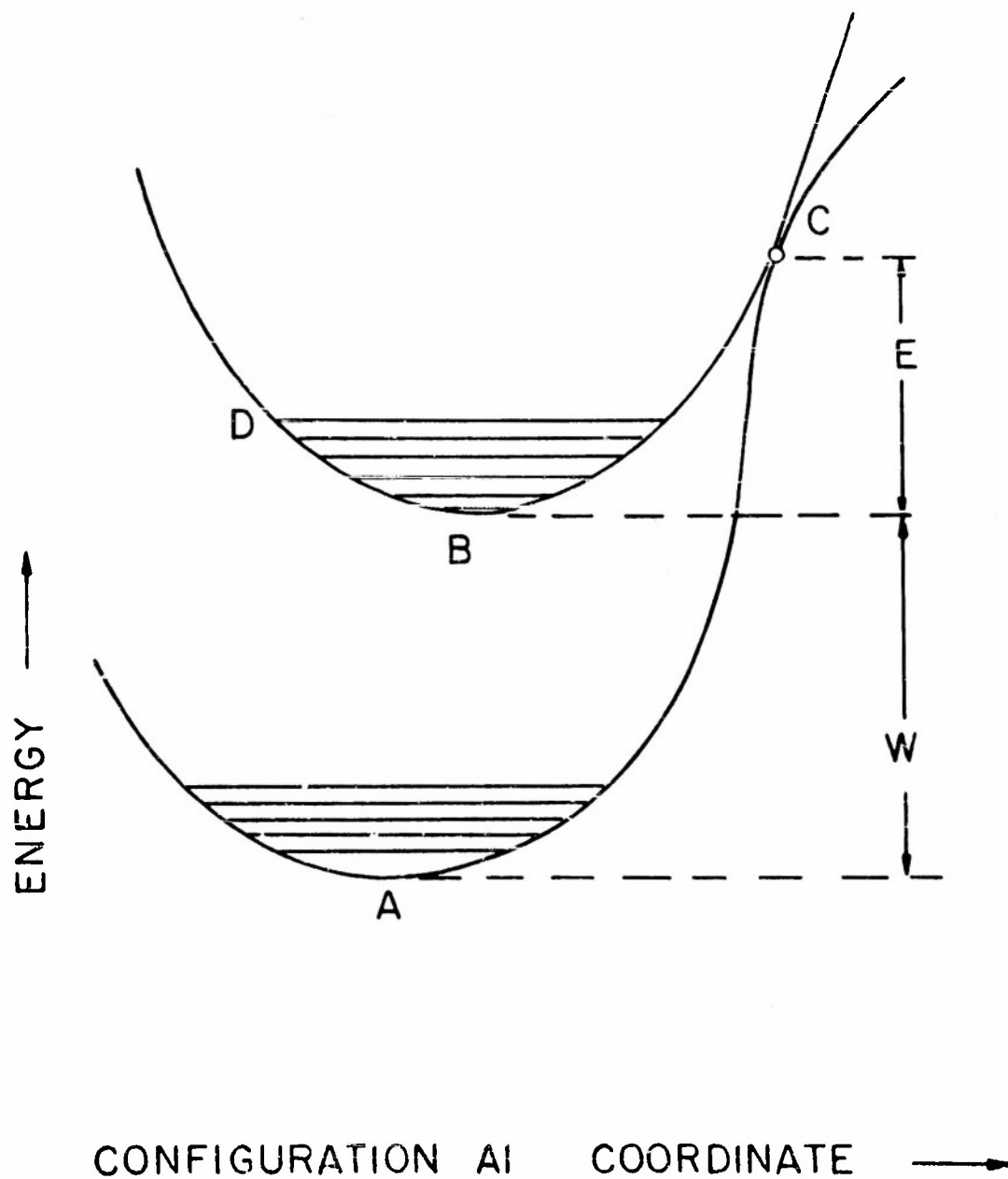


FIG. 1

TYPICAL EMISSION SPECTRUM AND
TEMPERATURE DEPENDENCE OF A
NON-PHOTOCONDUCTING PHOSPHOR

FIG. 2
ENERGY VS CONFIGURATION CURVES
FOR A LUMINESCENT CENTER



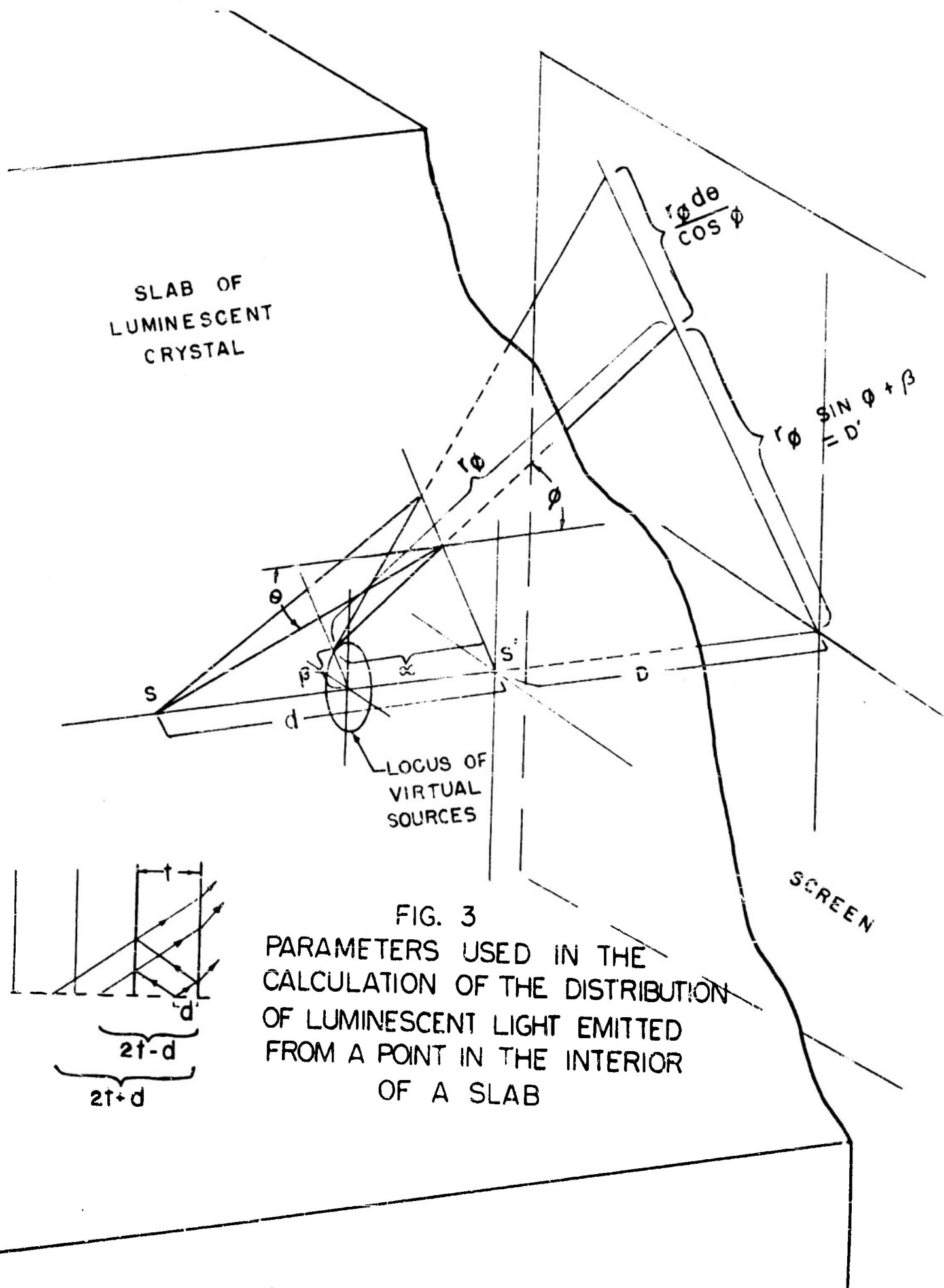


FIG. 4
LOCI OF VIRTUAL SOURCES
IN Ca WO_4

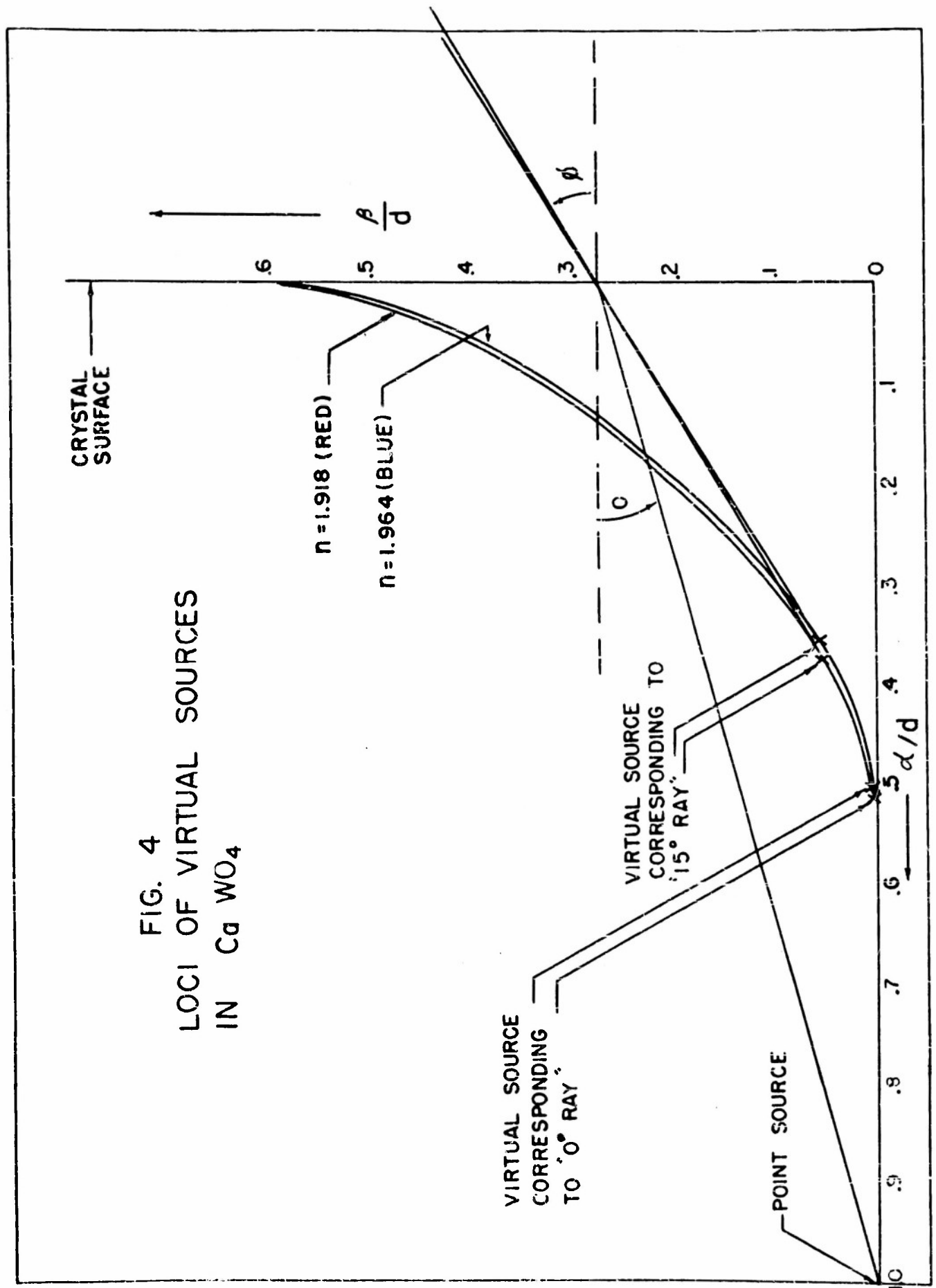
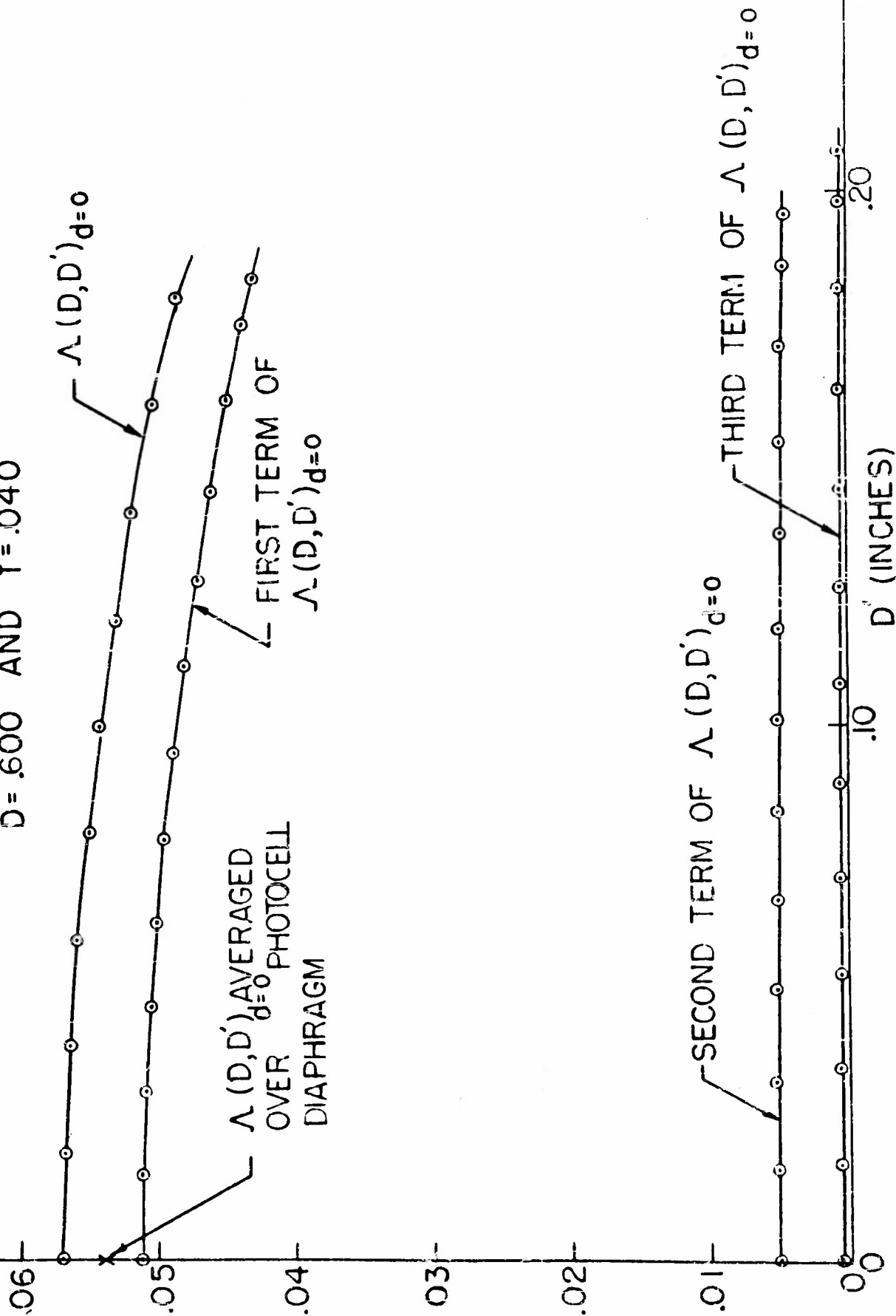


FIG 5

EQUATION 7, $\Lambda(D, D')$, COMPUTED

FOR 4358 Å, $n = 1.9639$, $I = 1$

$D = .600$ " AND $t = .040$ "



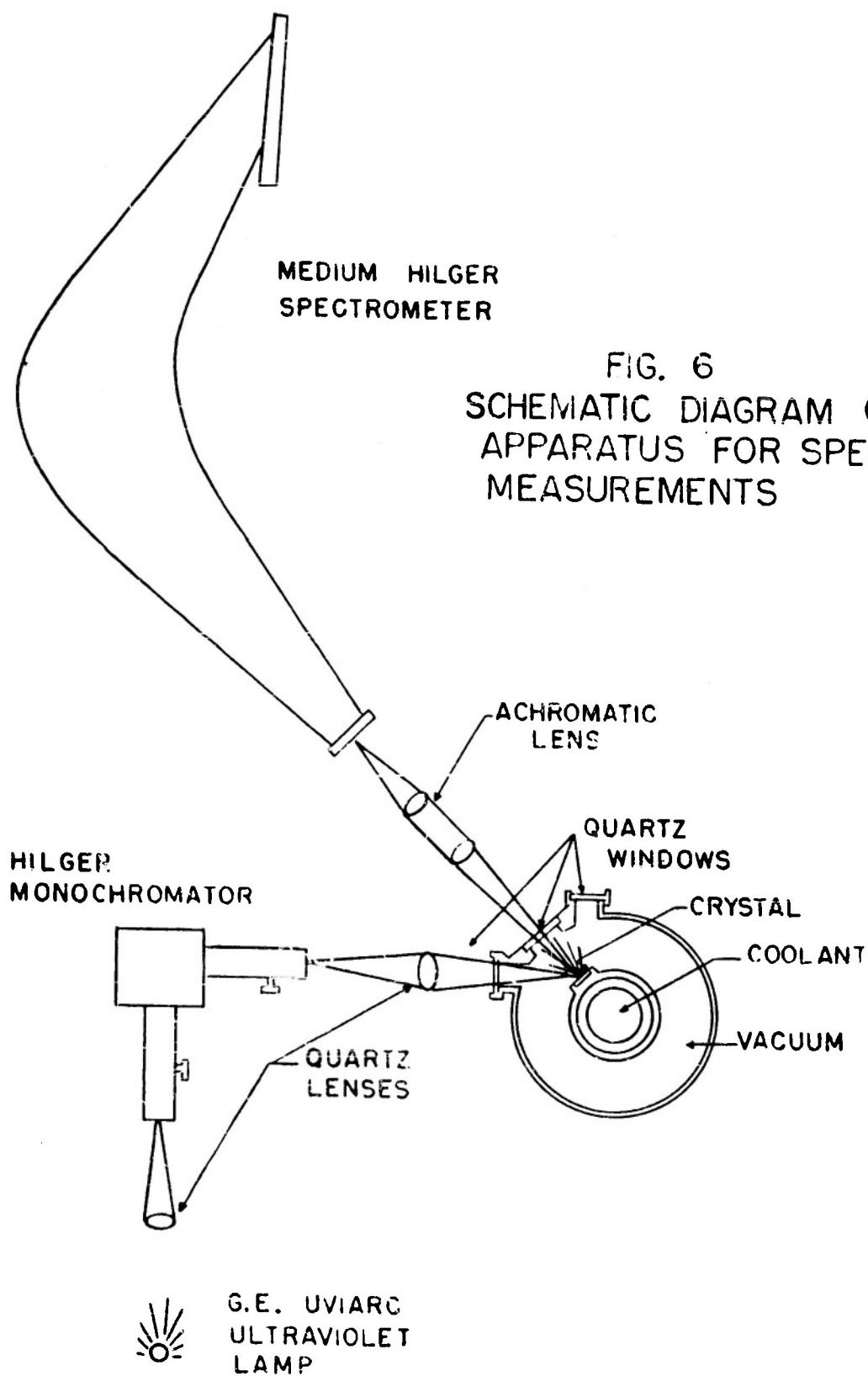


FIG. 6
SCHEMATIC DIAGRAM OF
APPARATUS FOR SPECTRUM
MEASUREMENTS

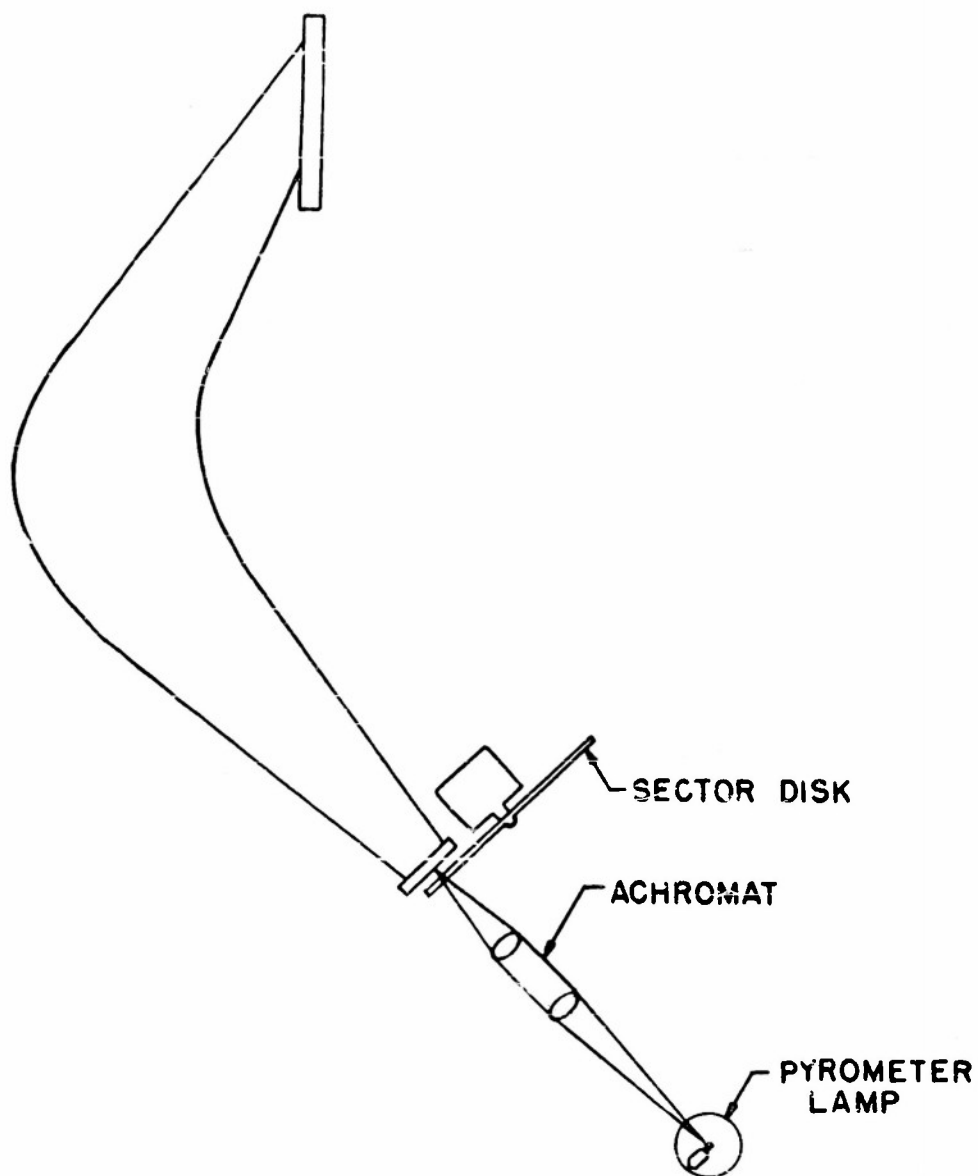


FIG 7
SCHEMATIC DIAGRAM OF
APPARATUS USED TO
CALIBRATE SPECTROMETER

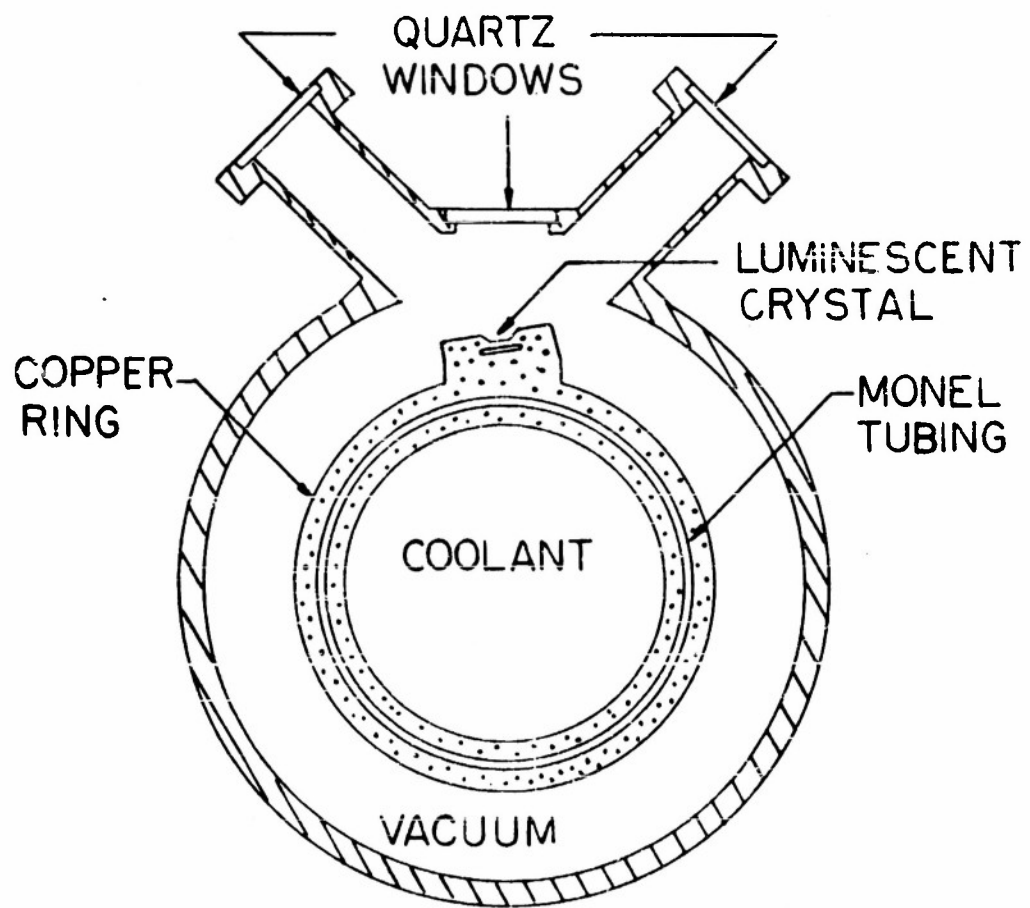
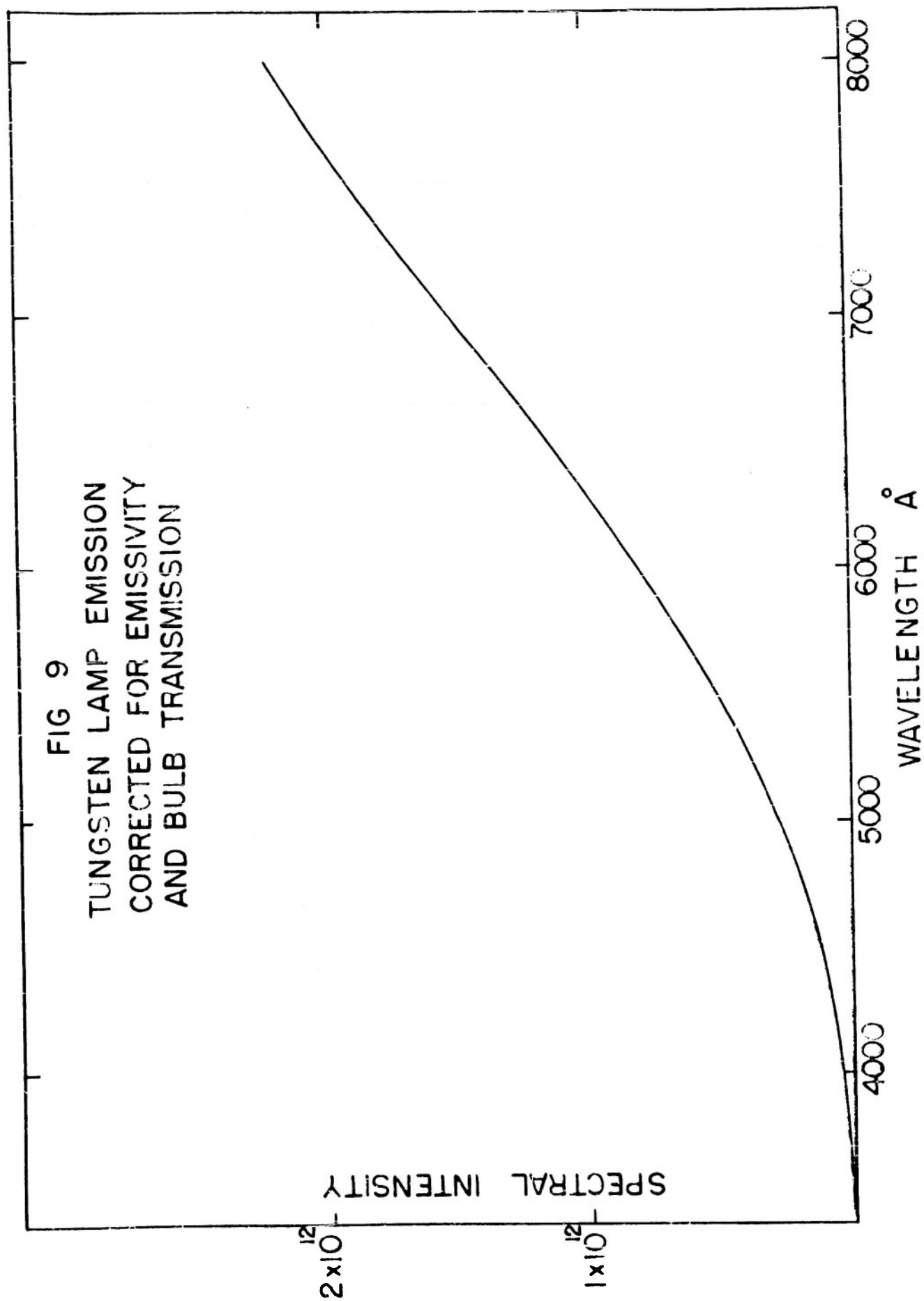


FIG 8
CROSS SECTION OF THE CRYOSTAT
USED TO MAINTAIN THE
CRYSTALS AT A FIXED TEMPERATURE

FIG 9
TUNGSTEN LAMP EMISSION
CORRECTED FOR EMISSIVITY
AND BULB TRANSMISSION



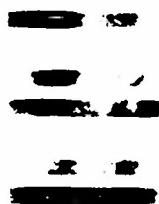


FIG 10
EXAMPLES OF THE PHOTOGRAPHIC
PLATES OBTAINED IN THE SPECTRUM
MEASUREMENTS

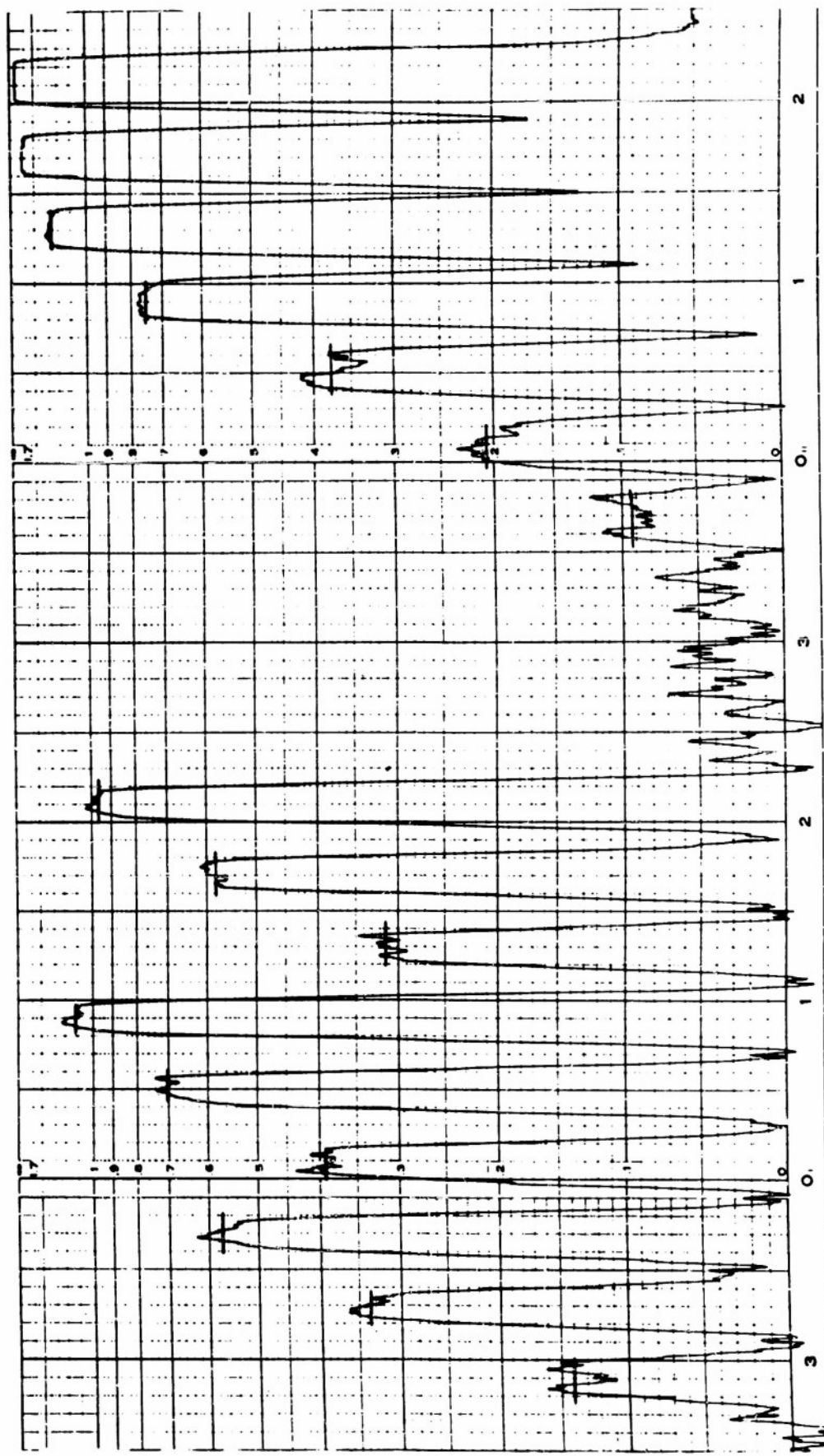


FIG 11

A DENSITOMETER TRACING OBTAINED
FROM ONE OF THE LUMINESCENT
SPECTRA PLATES

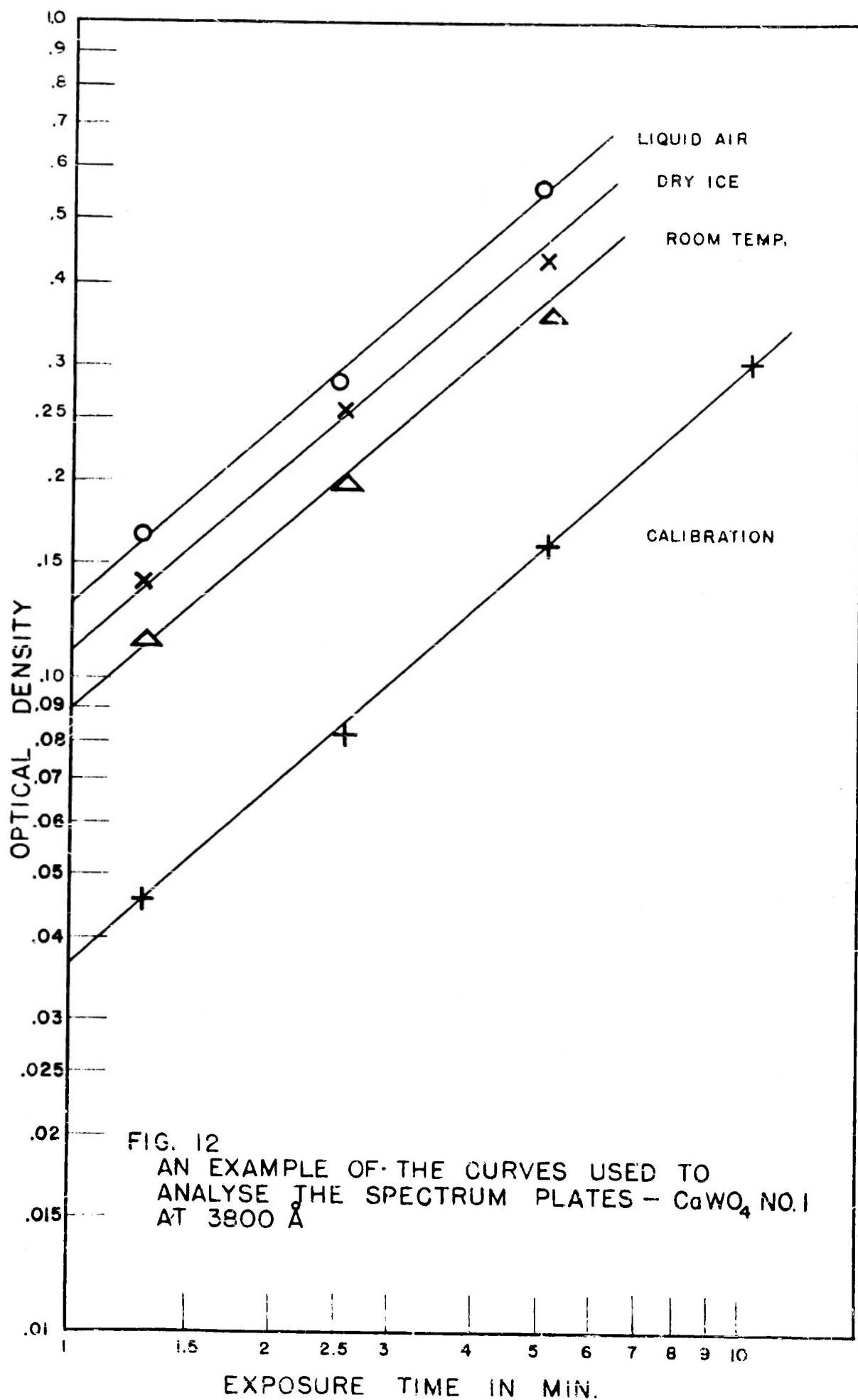




FIG. 13
PHOTOCELL AMPLIFIER CIRCUIT

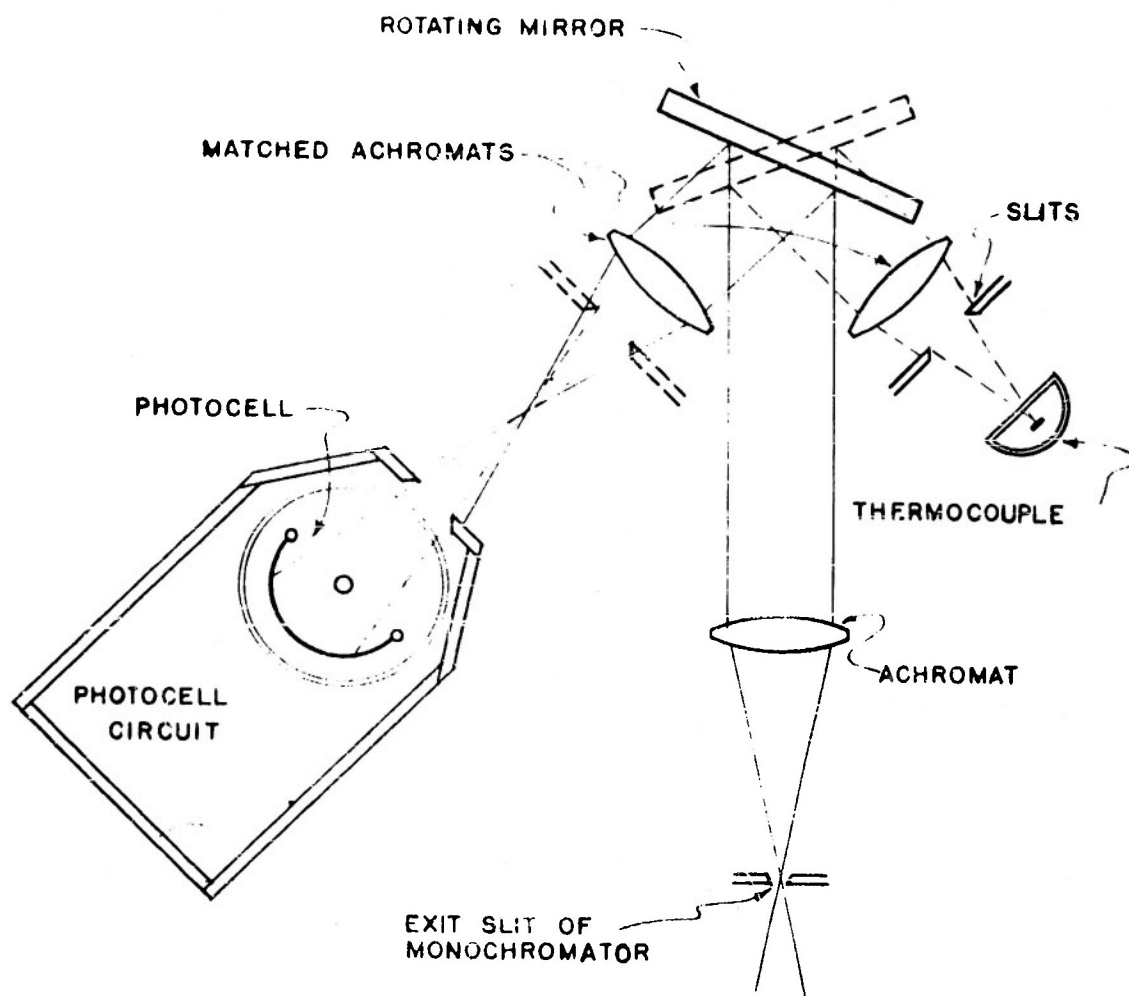
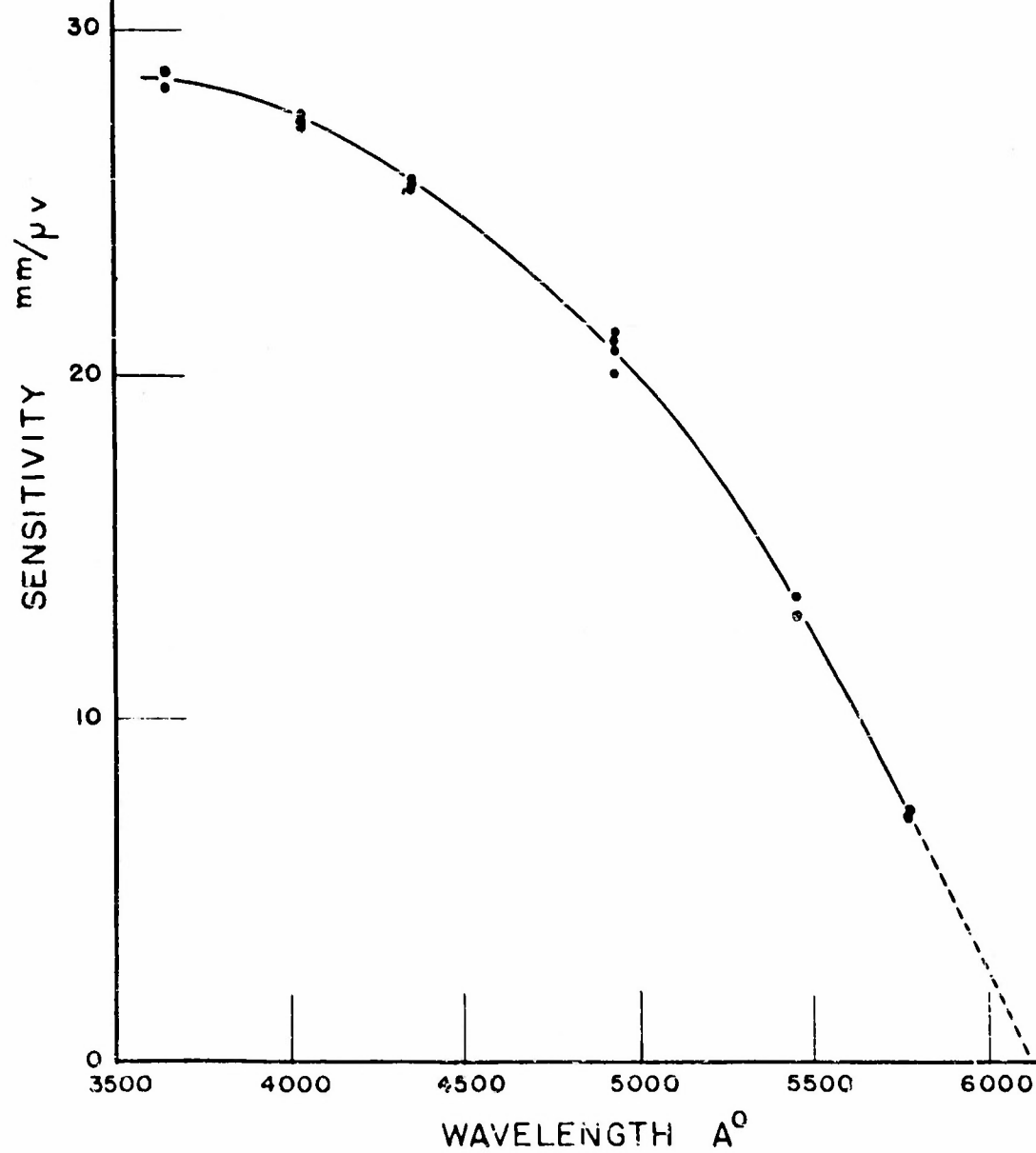


FIG. 14
SCHEMATIC ARRANGEMENT OF APPARATUS FOR
PHOTOCELL CALIBRATION

FIG. 15
PHOTOCELL CALIBRATION CURVE



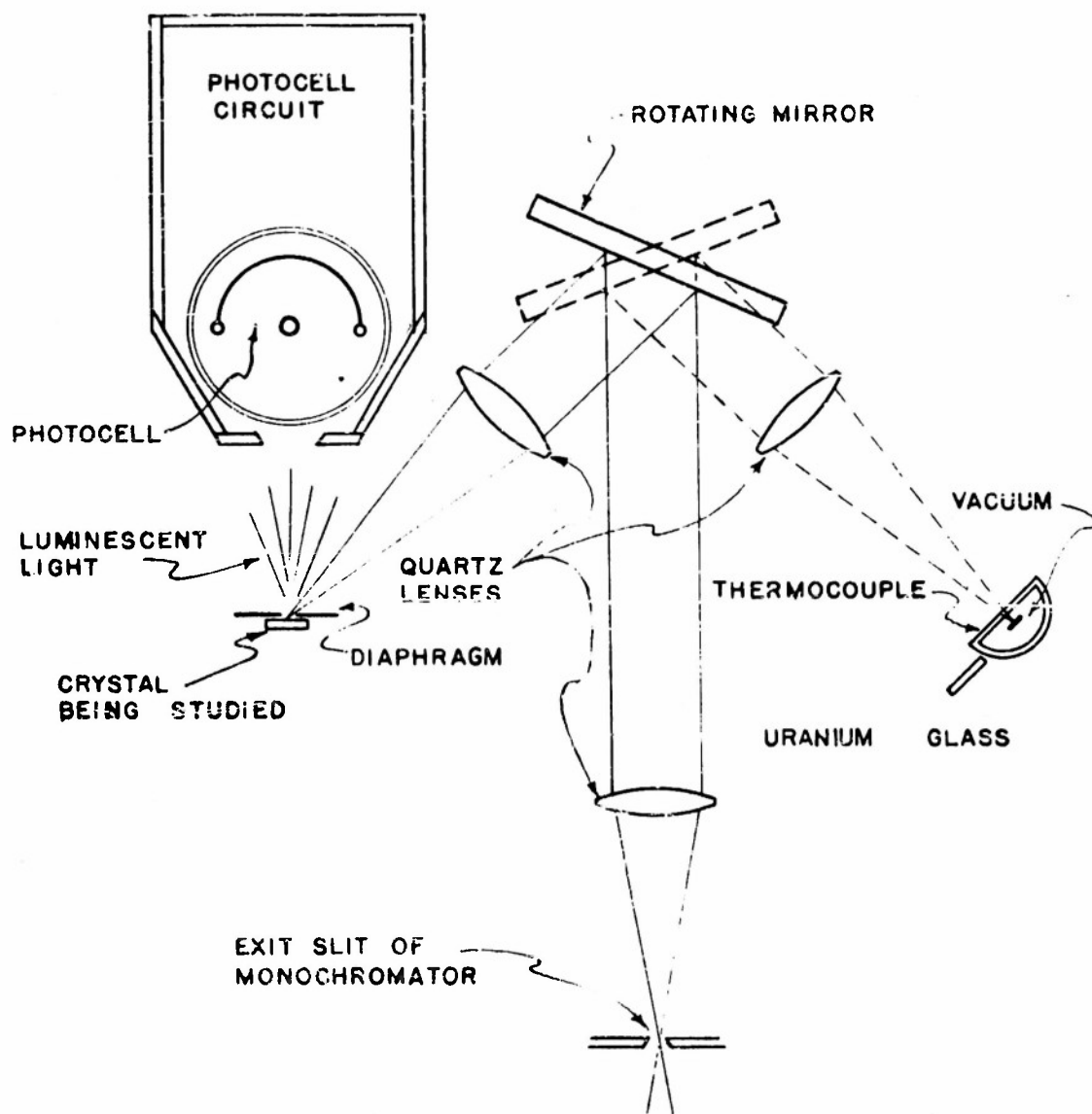


FIG. 16
SCHEMATIC ARRANGEMENT OF APPARATUS FOR
EFFICIENCY MEASUREMENTS

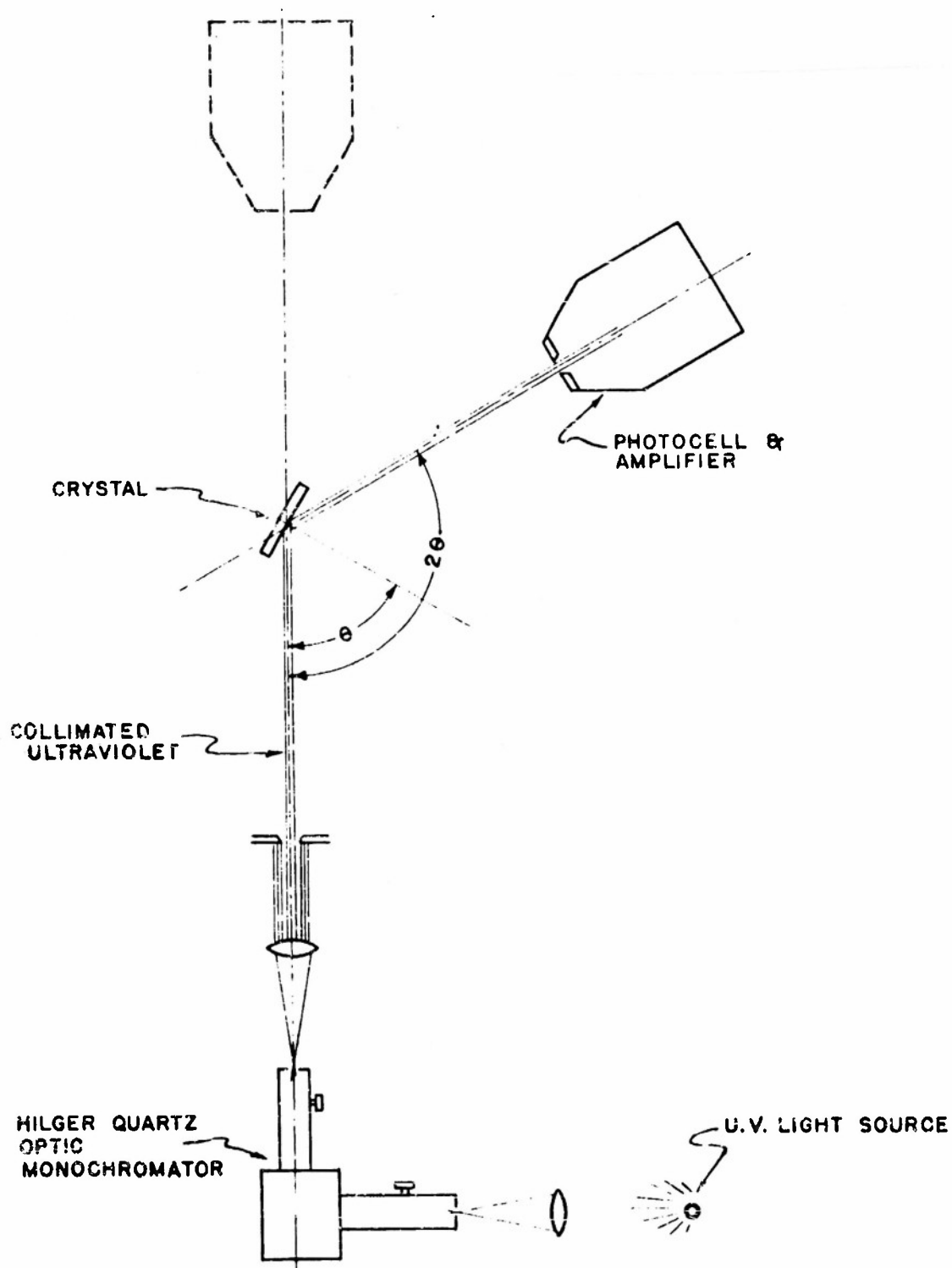


FIG. 17
APPARATUS FOR REFLECTION MEASUREMENTS

FIG. 18
REFLECTION OF 2537Å^o ULTRA-VIOLET
FROM CaWO_4 CRYSTALS

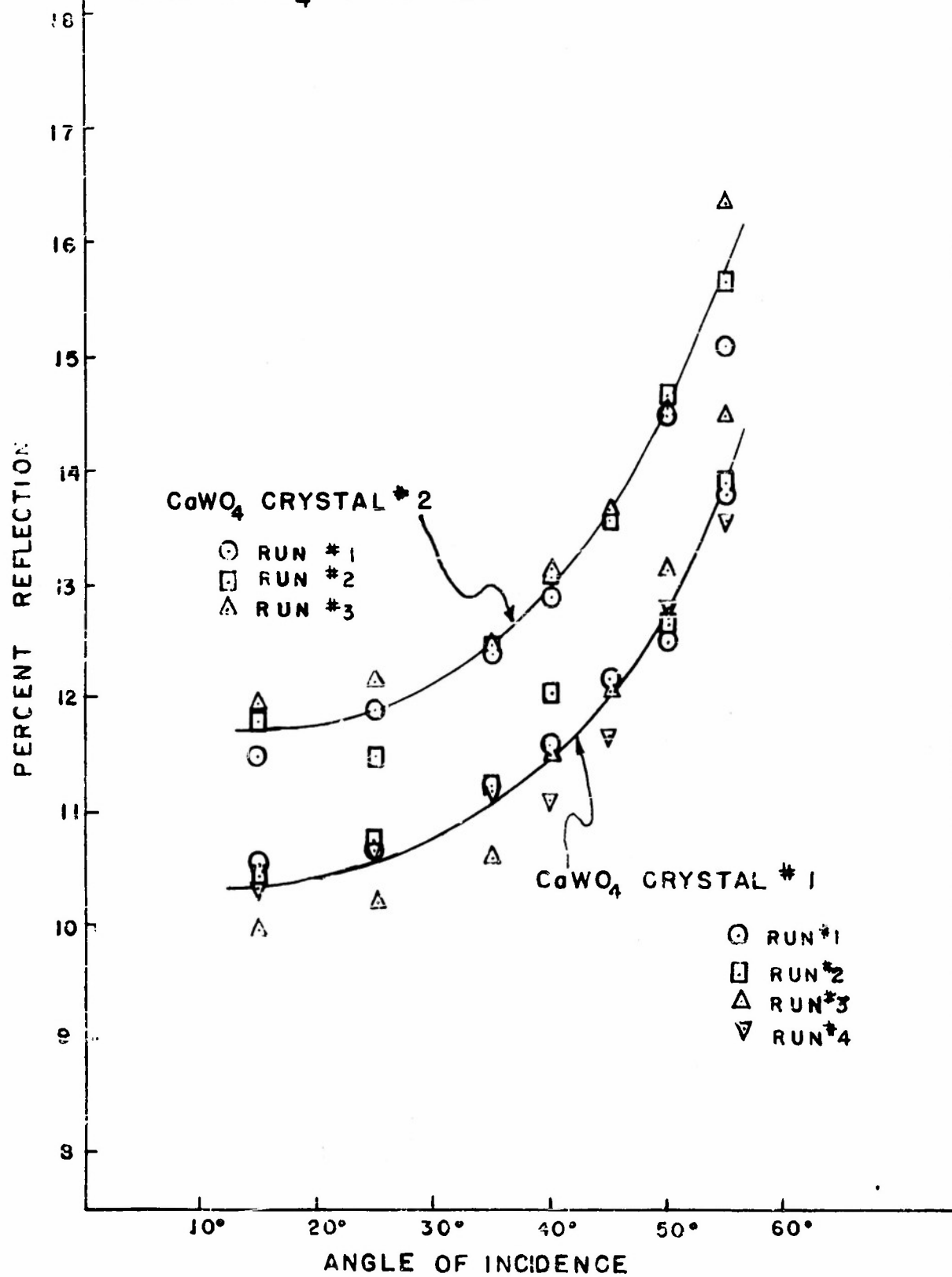


FIG. 19
 CdWO_4 REFLECTION DATA

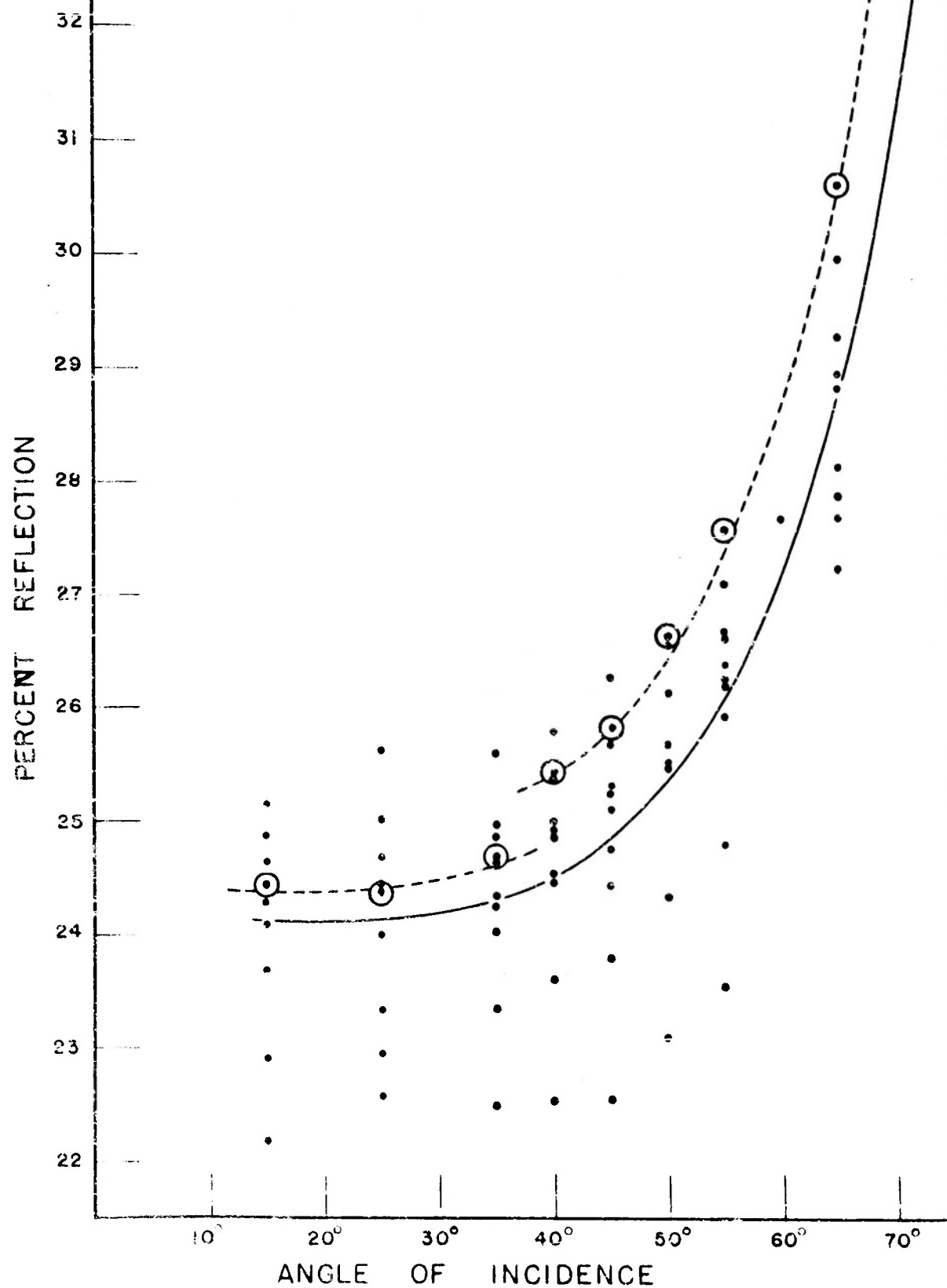


FIG. 20
REFLECTION OF 2537 Å⁰ ULTRA-VIOLET
FROM CeWO_4 CRYSTALS

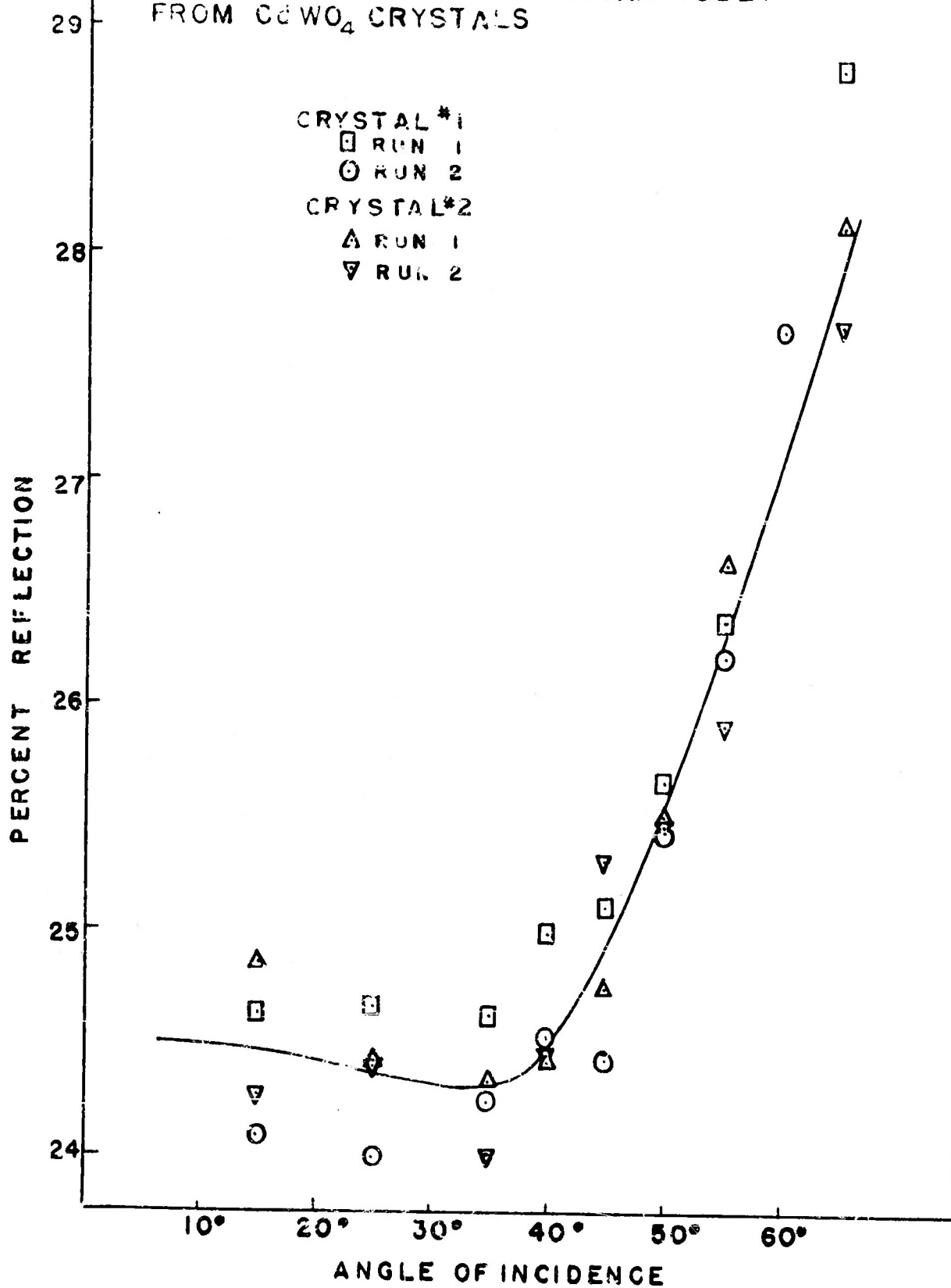


FIG. 21
OPTICAL TRANSMISSION OF CdWO_4 CRYSTALS

○ CRYSTAL #1
△ CRYSTAL #2

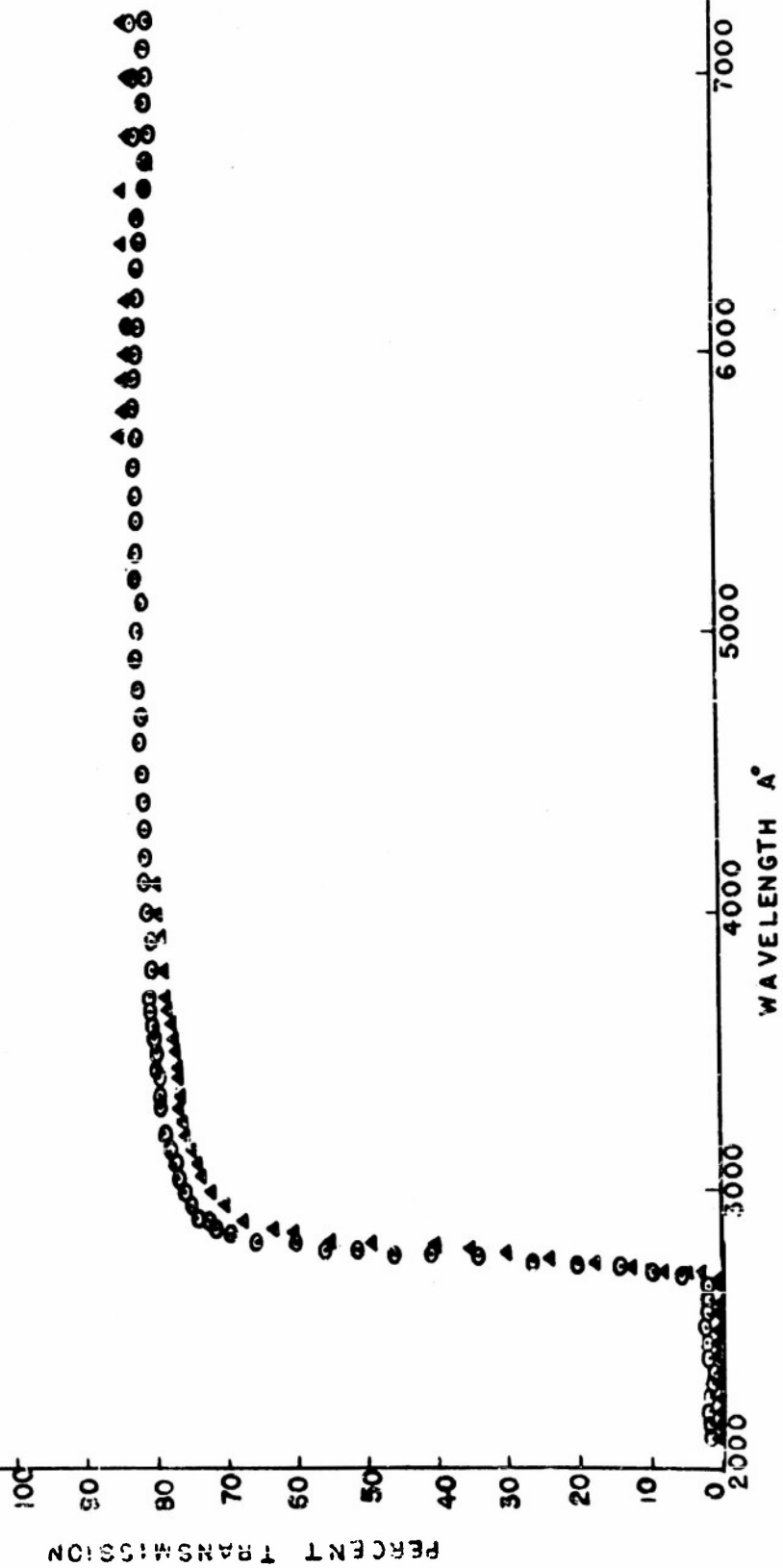


FIG. 22
OPTICAL TRANSMISSION OF CaWO_4 IN THE
CUTOFF REGION

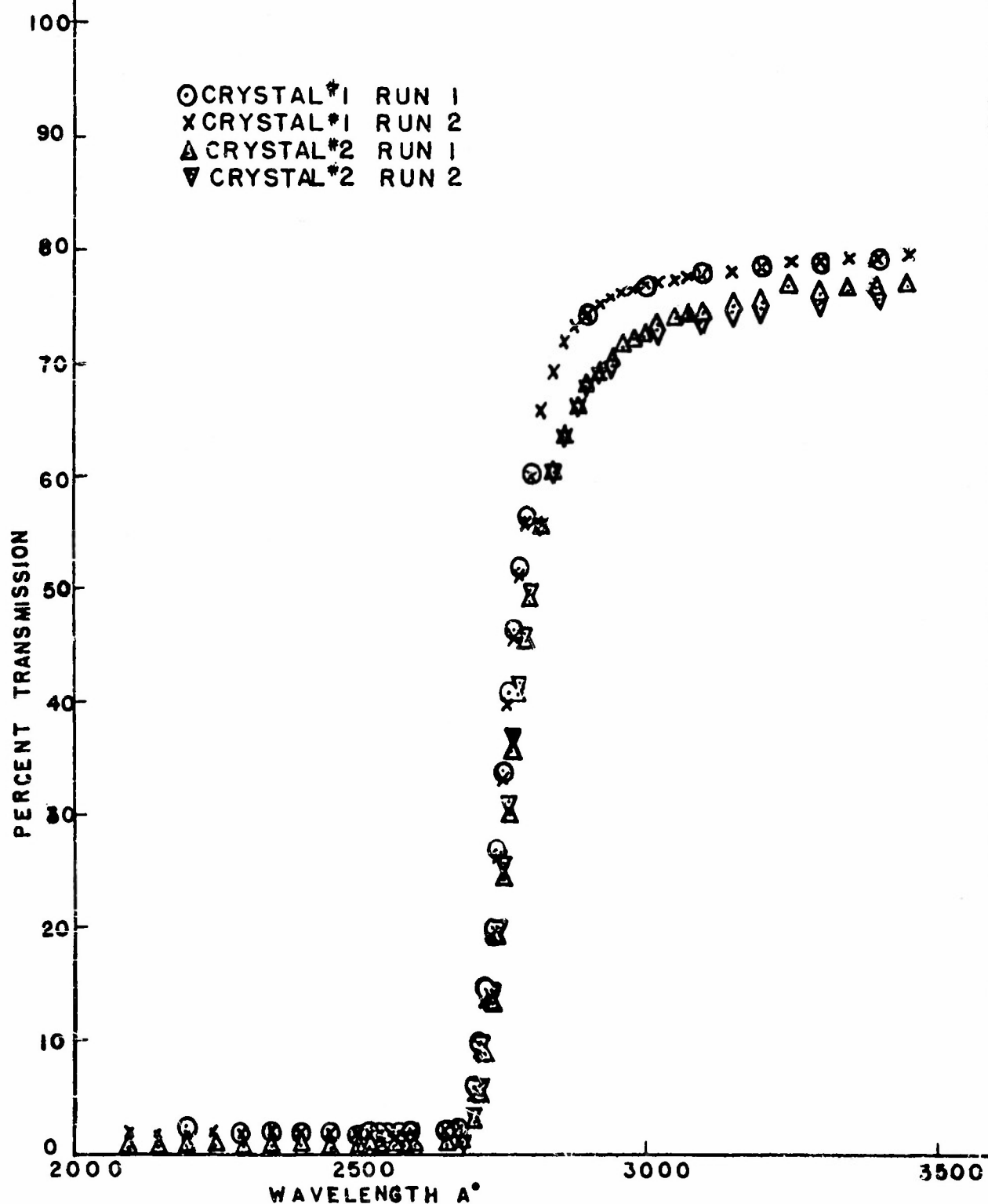


FIG. 23
TRANSMISSION OF CaWO_4 CRYSTAL #2 NEAR 2537 \AA

○ CRYSTAL ONLY: RUN 1
 × CRYSTAL ONLY: RUN 2
 * FILTER ONLY
 △ CRYSTAL PLUS FILTER: RUN 1

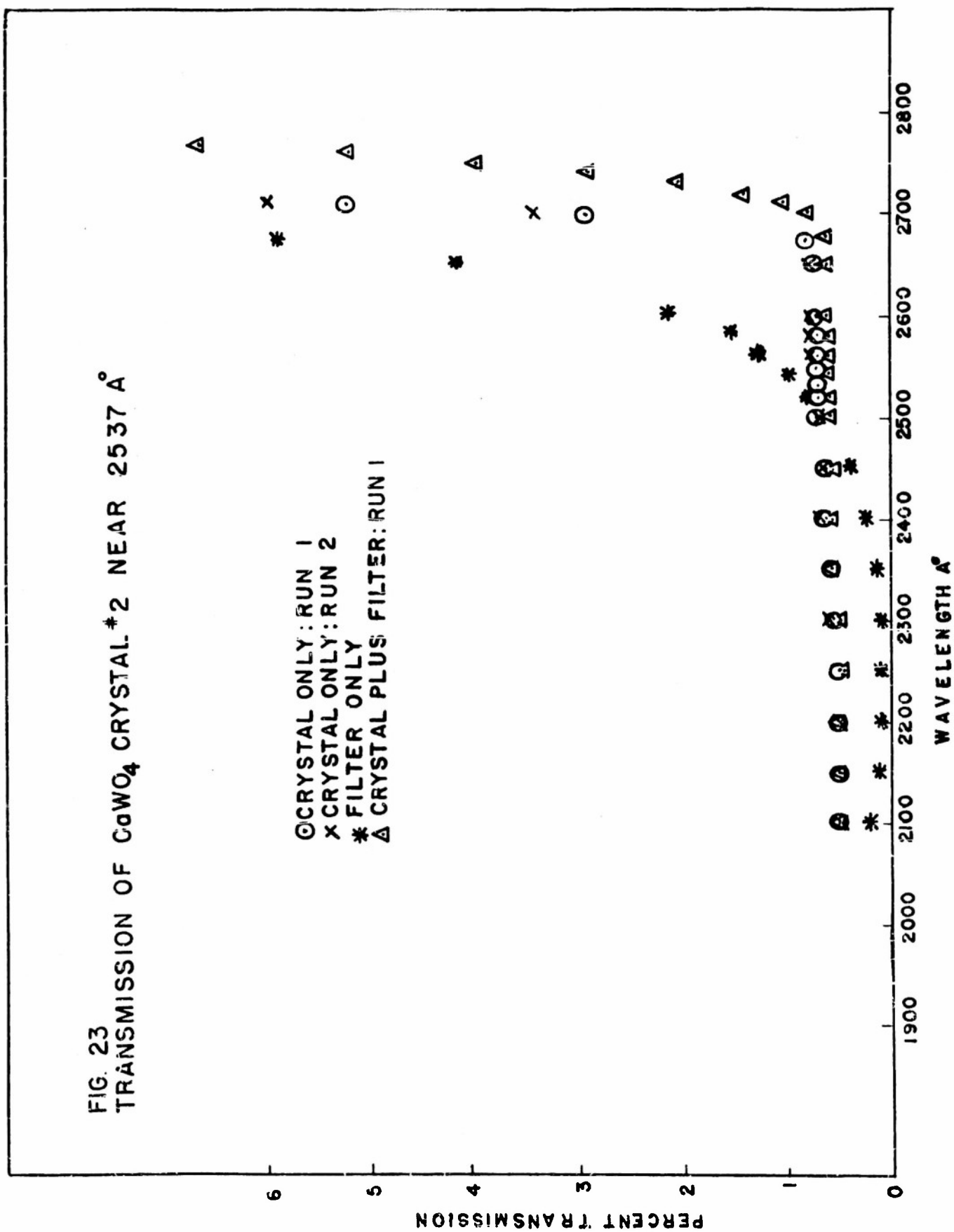


FIG. 24
TRANSMISSION OF CaWO_4 CRYSTAL #1 NEAR 2537 Å

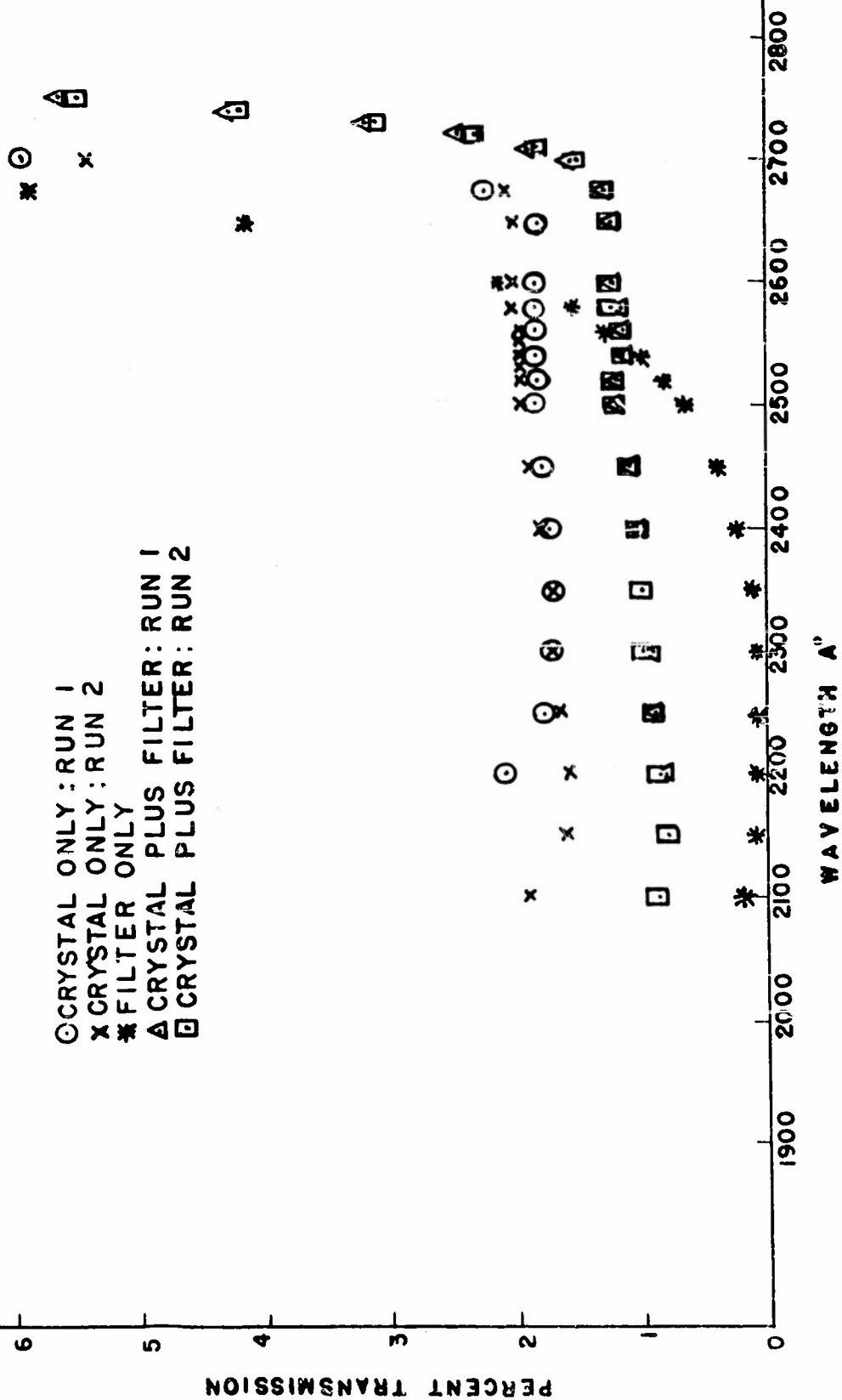


FIG. 25
OPTICAL TRANSMISSION OF CdWO_4 CRYSTALS

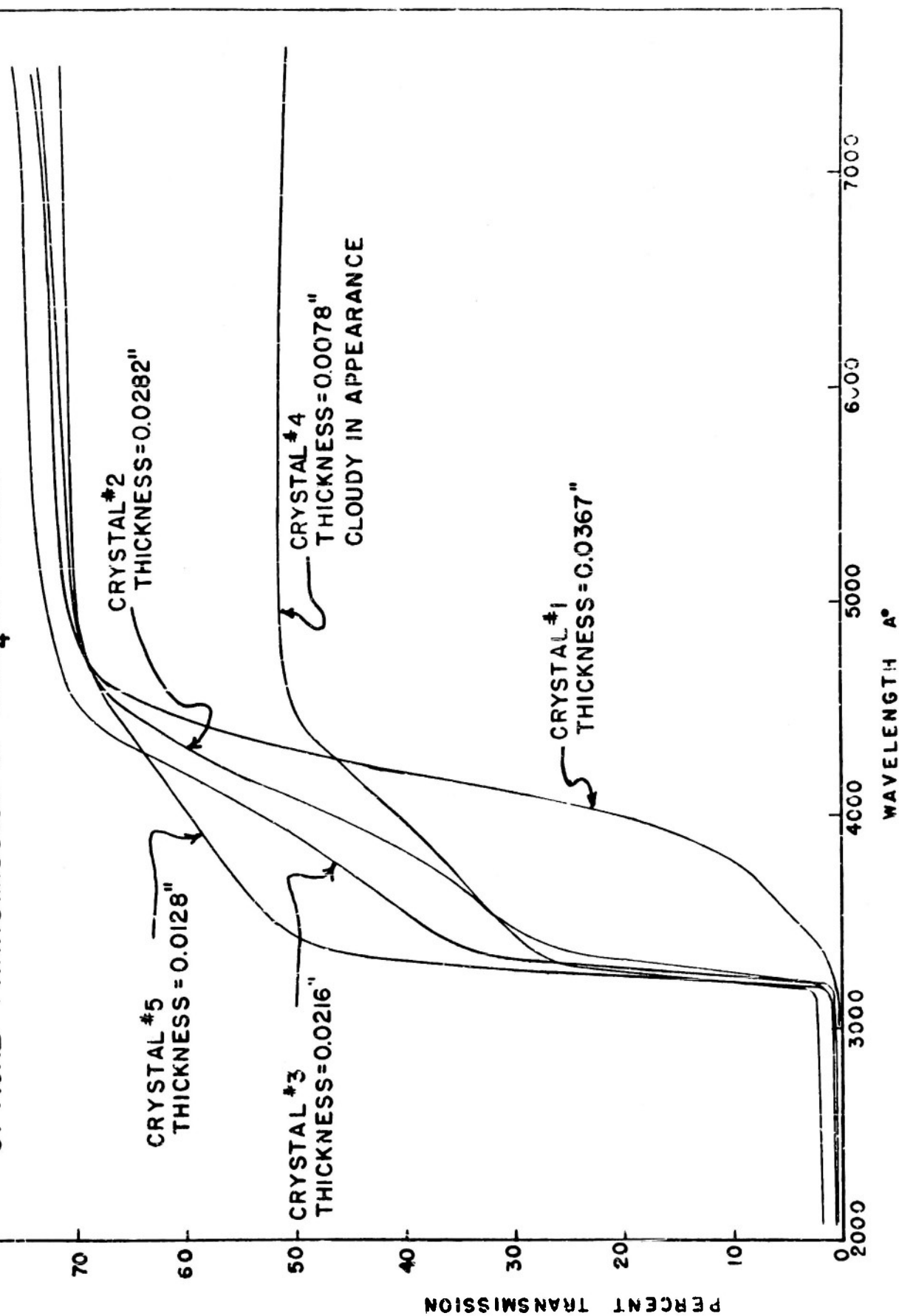


FIG. 26
 DETAIL OF THE CdWO_4 TRANSMISSION
 FROM 2100 TO 3500 \AA

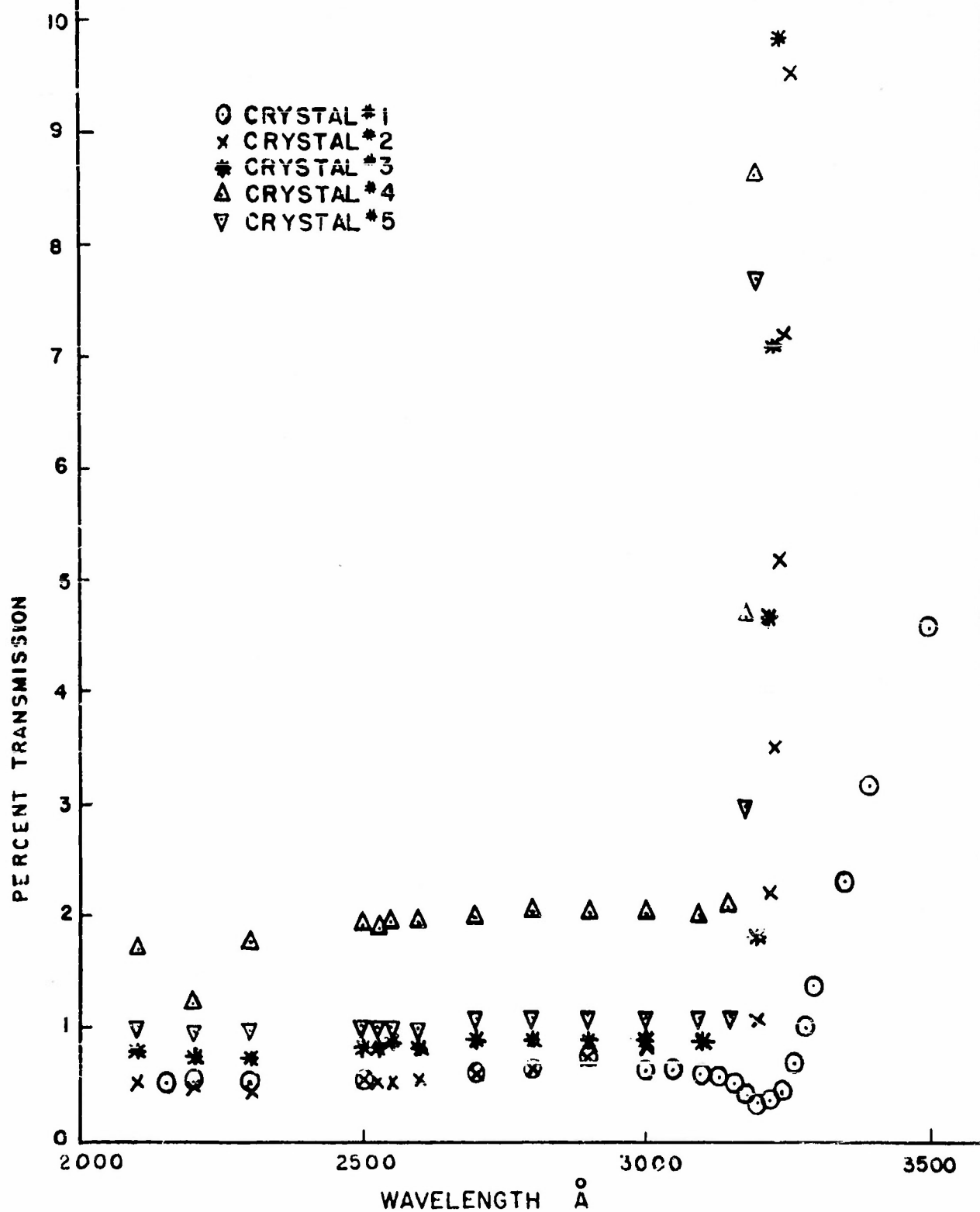


FIG. 27
DETAIL OF THE CdWO_4 TRANSMISSION
FROM 3000 TO 4500 \AA

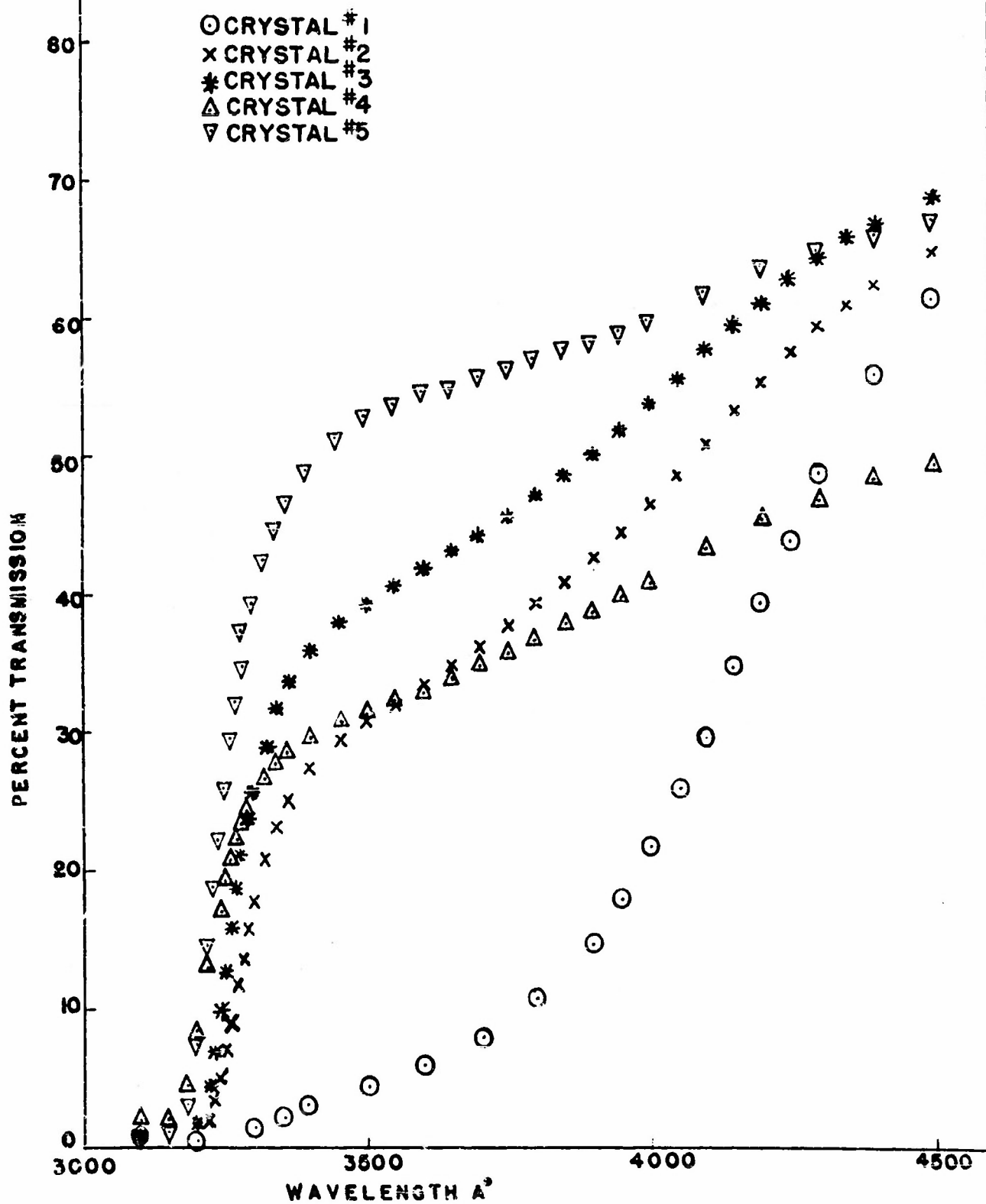


FIG. 28
LUMINESCENT SPECTRA MEASUREMENTS ON CdWO_4 AT ROOM TEMPERATURE

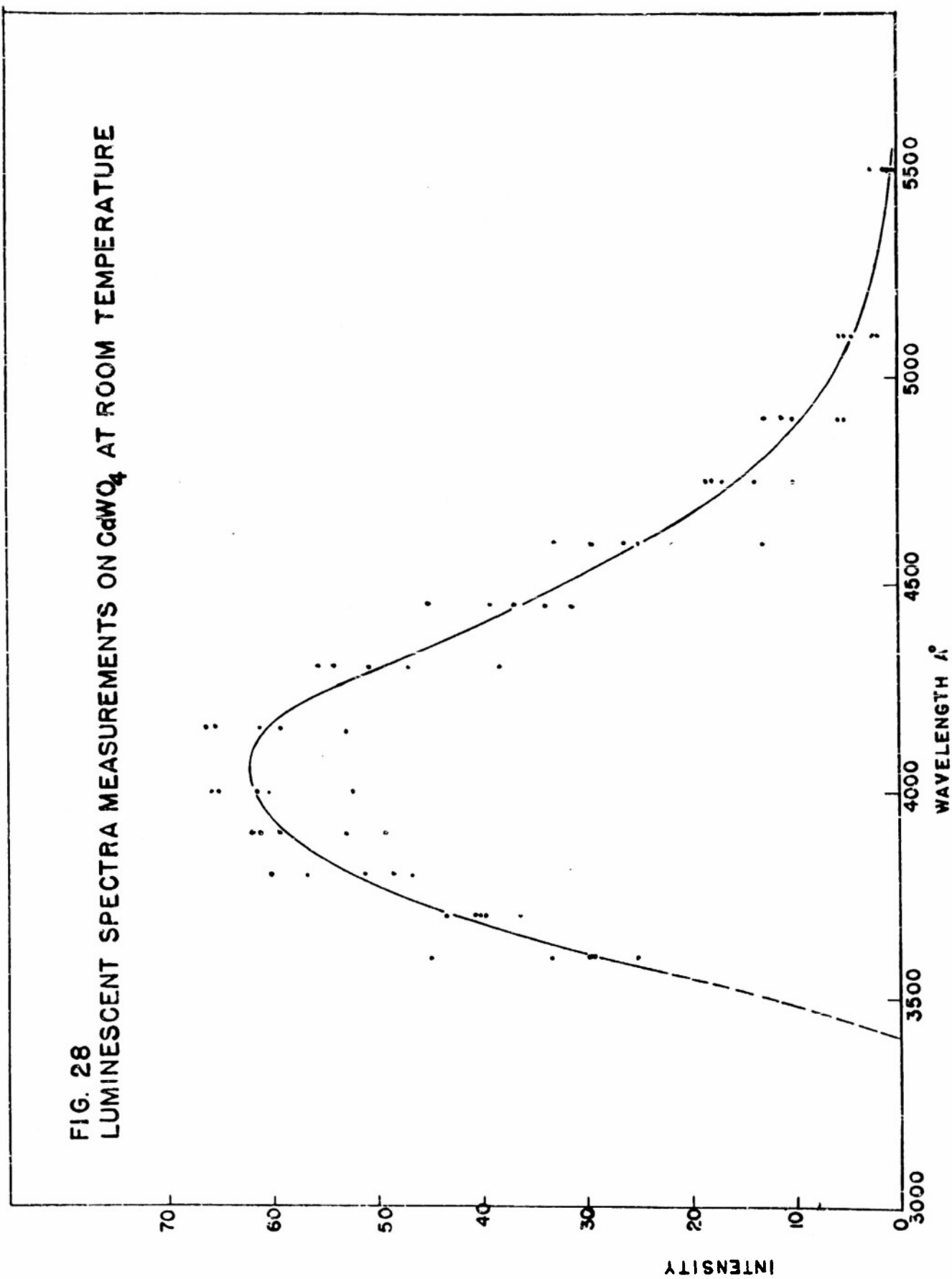


FIG. 29
LUMINESCENT SPECTRA MEASUREMENTS ON CoWO_4 AT DRY ICE
TEMPERATURE

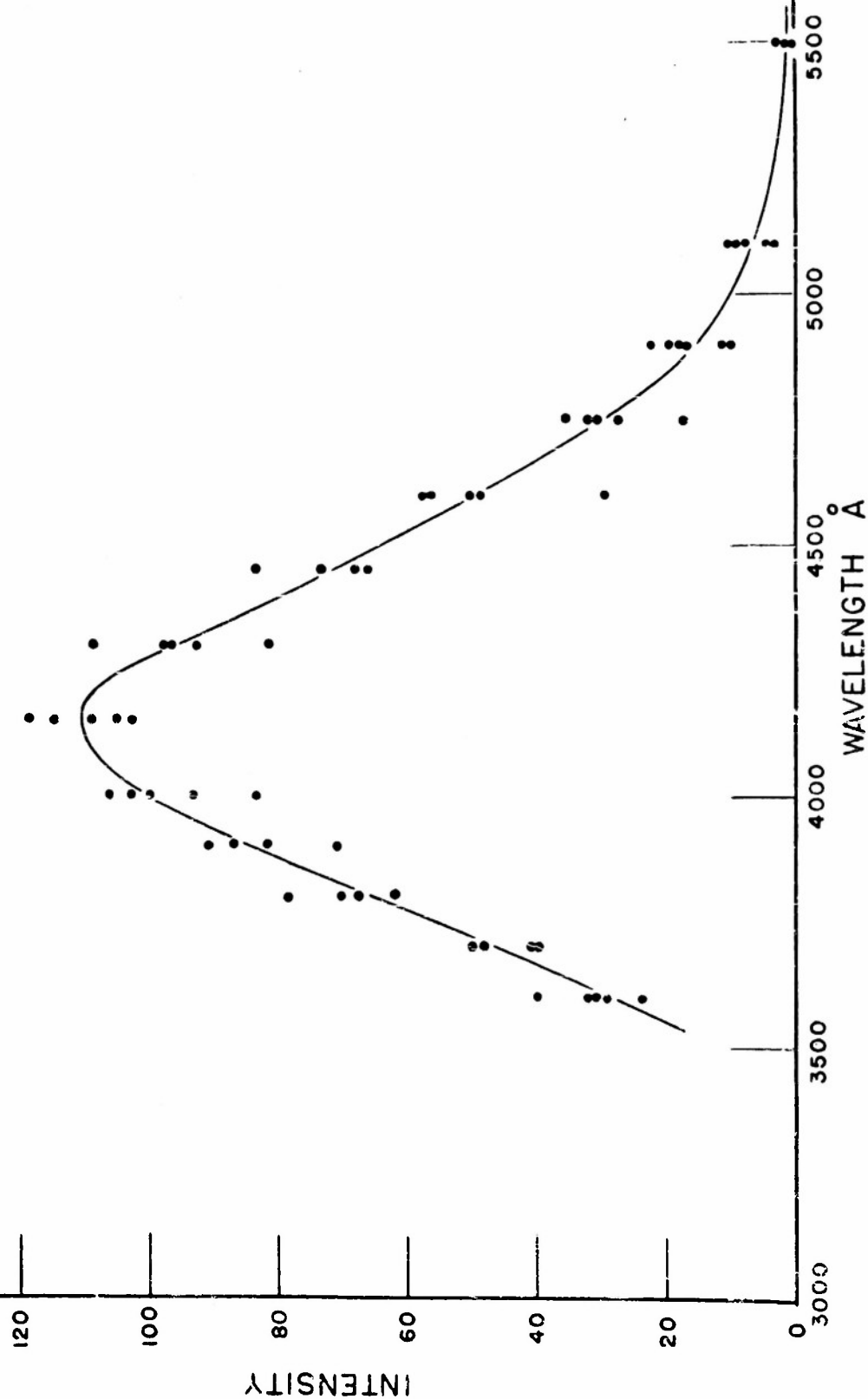


FIG. 30
LUMINESCENT SPECTRA OF CdWO_4 AND LIQUID AIR DATA

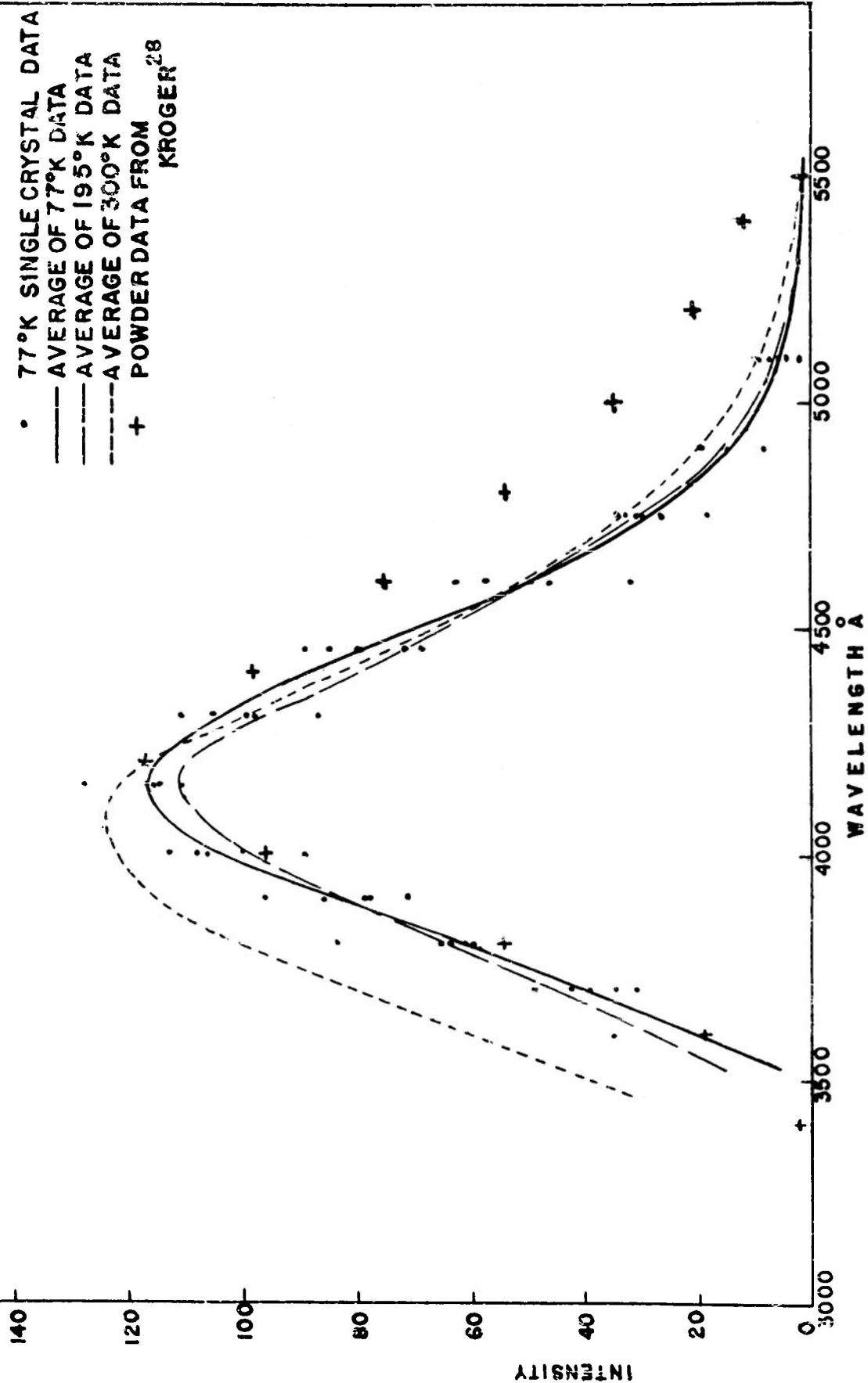


FIG. 31
LUMINESCENT SPECTRA MEASUREMENTS ON CdWO_4 AT ROOM
TEMPERATURE

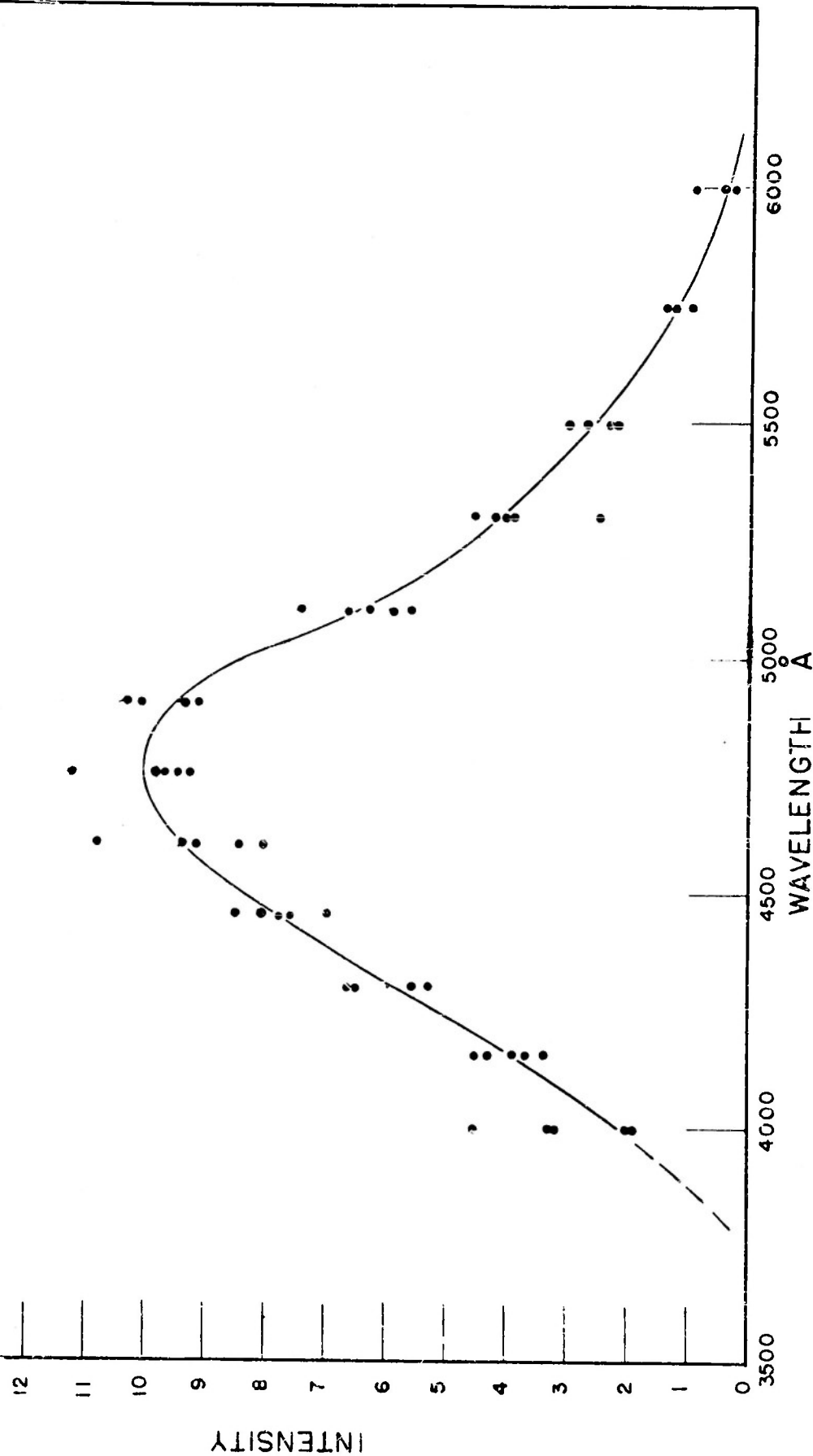


FIG. 32
LUMINESCENT SPECTRA MEASUREMENTS ON CdWO_4 (AT DRY ICE
TEMPERATURES)

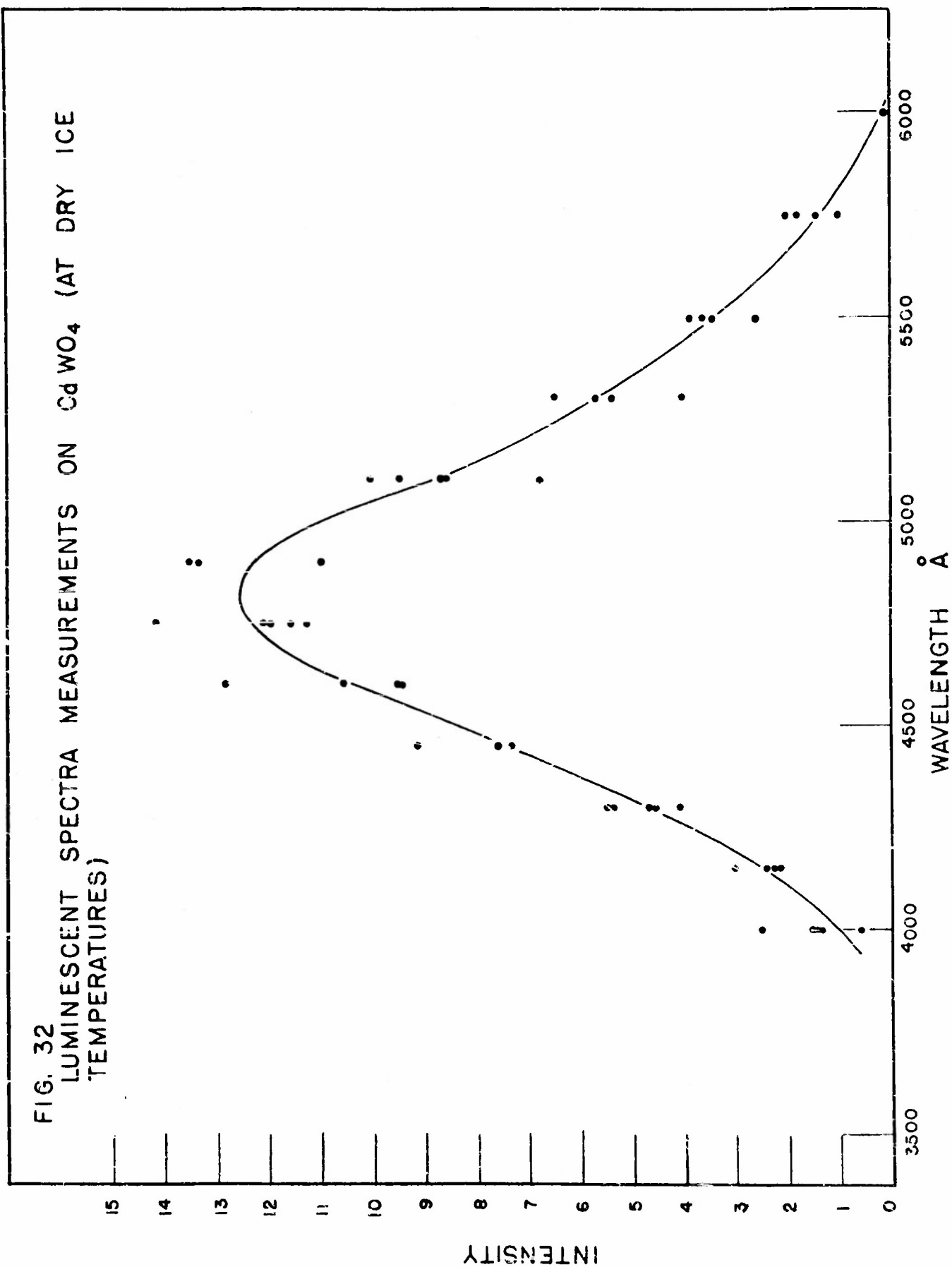


FIG. 33
LUMINESCENT SPECTRA MEASUREMENTS ON CdWO_4 AT LIQUID
 N_2 TEMPERATURES

• SINGLE CRYSTAL DATA
+ KROGER 28

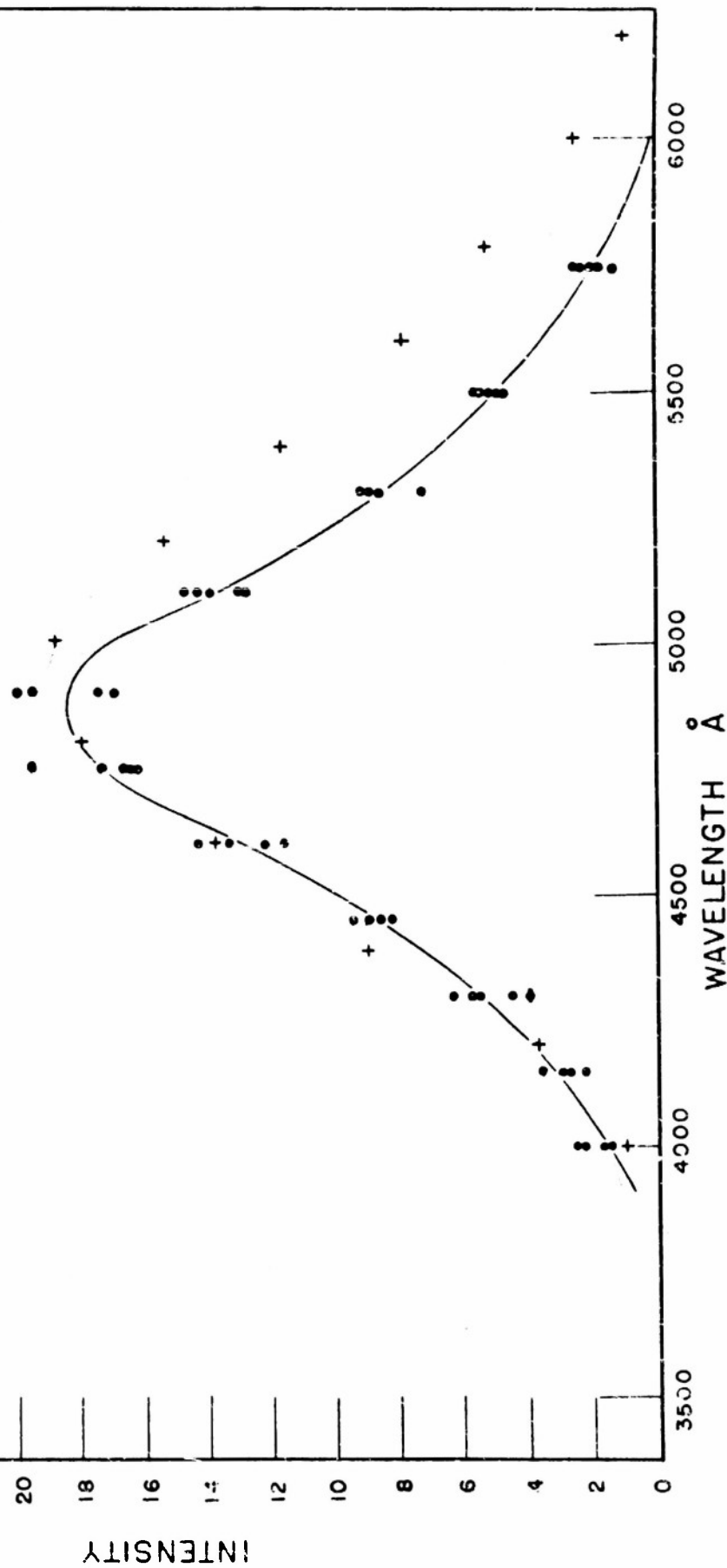


FIG. 34
 CaWO_4 ROOM TEMPERATURE SPECTRA AS OBSERVED
AND CORRECTED TO THE CRYSTAL INTERIOR-
CURVES MATCHED AT PEAK

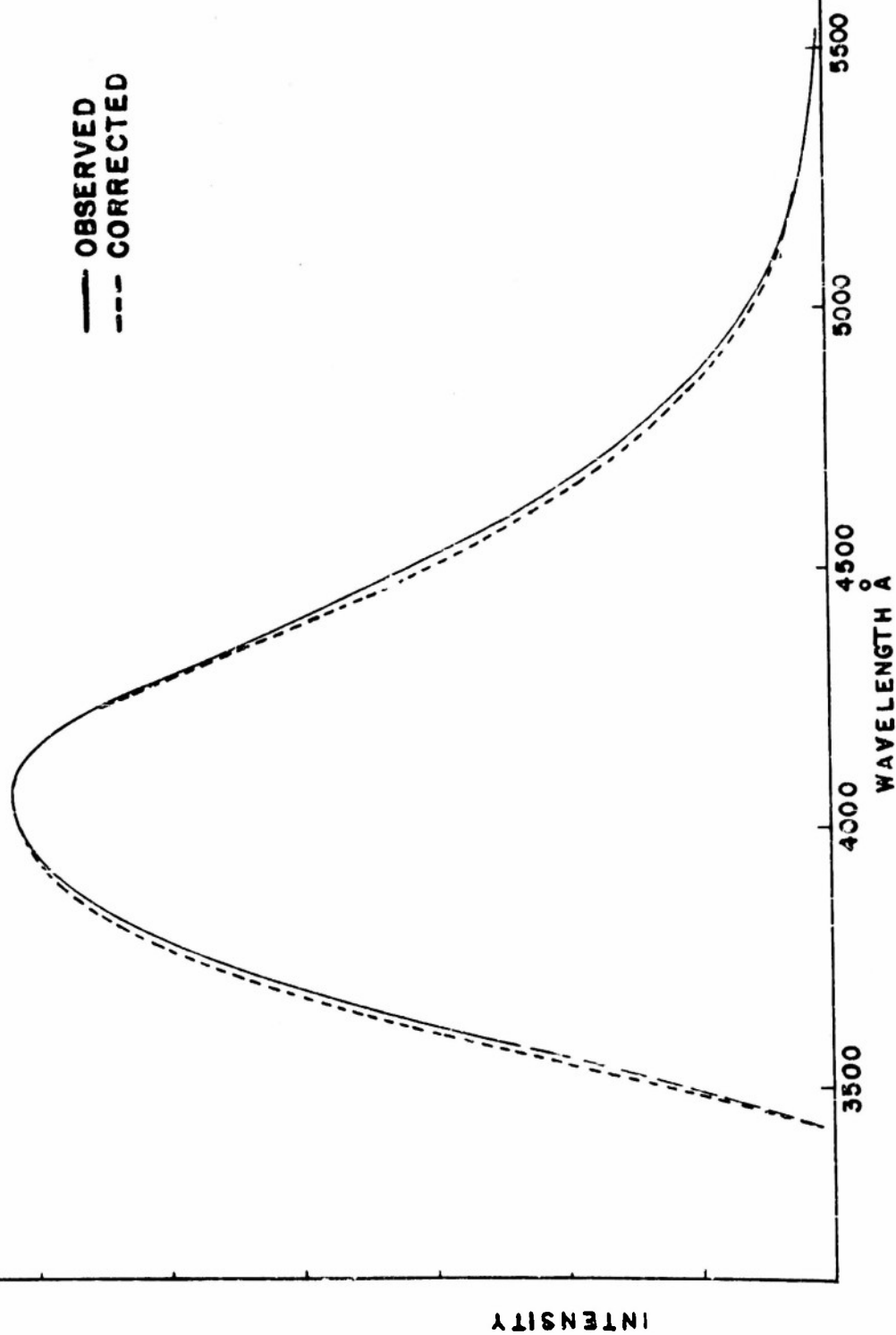


FIG. 35
DEPENDENCE OF THE LUMINESCENT EFFICIENCY
OF CaWO_4 ON TEMPERATURE

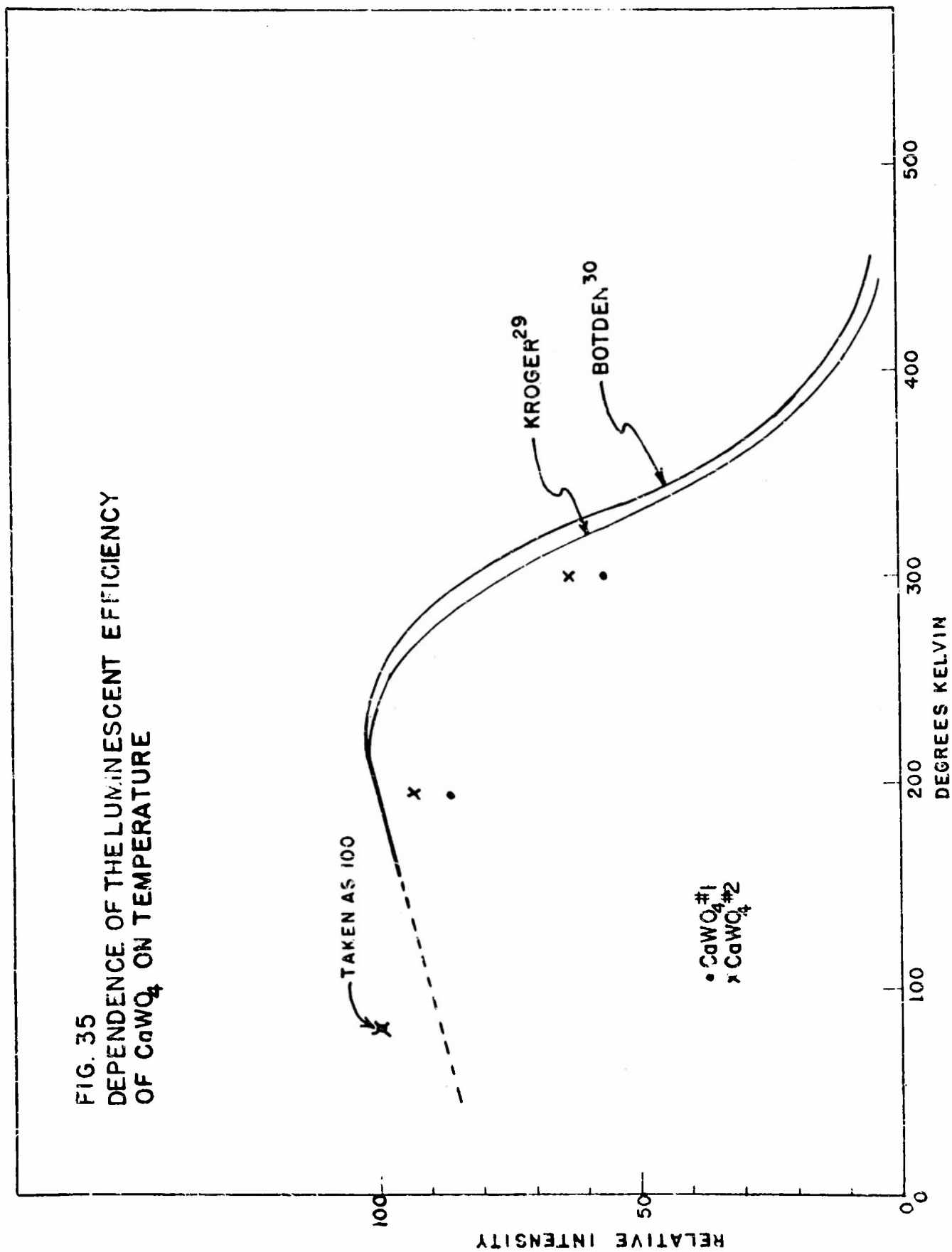


FIG. 36
DEPENDENCE OF THE LUMINESCENT EFFICIENCY
OF CdWO_4 ON TEMPERATURE

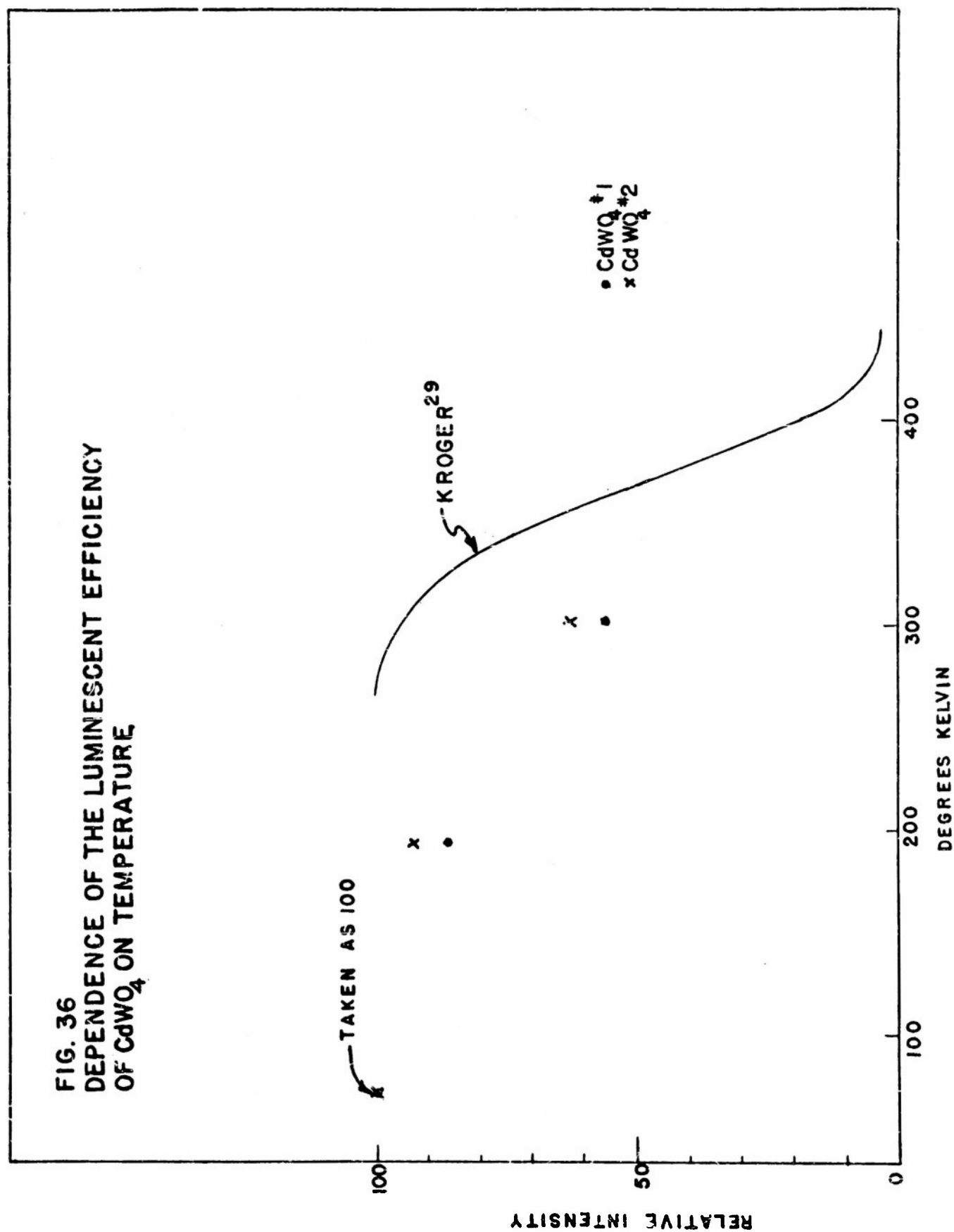
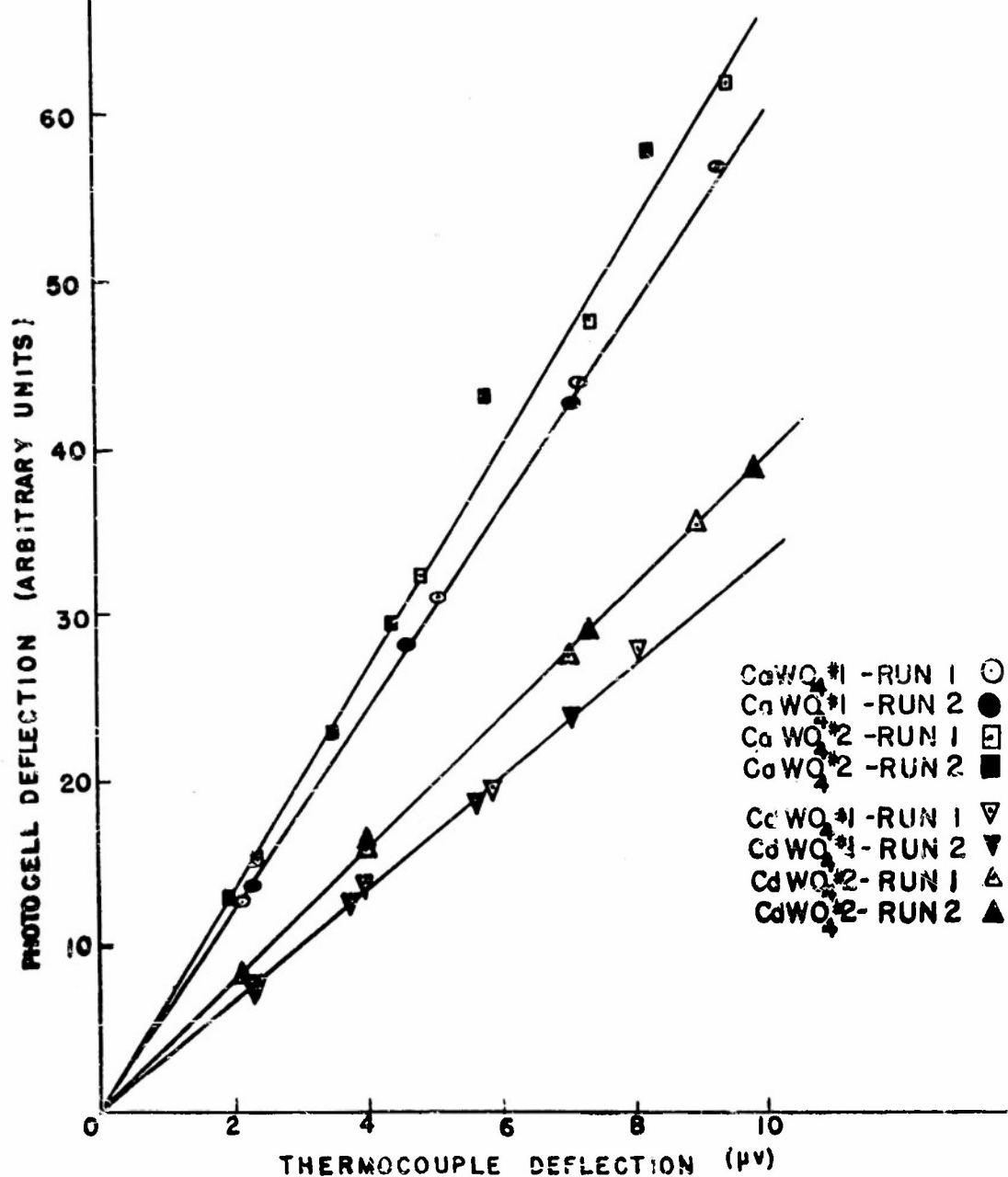


FIG. 37
ENERGY CONVERSION DATA SHOWING DEPENDENCE OF
LUMINESCENT EMISSION ON INTENSITY OF EXCITING
2537Å ULTRA-VIOLET



REFERENCES

1. Garlick, G.F.J., Luminescent Materials, Clarendon, Oxford, 1949.
 - 1a. Garlick, G.F.J., op. cit., 32 f.f.
 - 1b. Garlick, G.F.J., op. cit., 93 f.f.
2. Leverenz, H.W., Introduction to Luminescence of Solids, New York, Wiley, 1950.
 - 2a. Leverenz, H.W., op. cit., 88.
 - 2b. Leverenz, H.W., op. cit., 312 f.f.
3. Fonda, G.R. and Seitz, F., Conference on Luminescence, Cornell University, 1946, New York, Wiley, 1948.
4. Kröger, F., Some Aspects of the Luminescence of Solids, New York, Elsevier, 1948.
 - 4a. Kröger, F., op. cit., 107 f.f.
 - 4b. Kröger, F., op. cit., 113
 - 4c. Kröger, F., op. cit., 118
 - 4d. Kröger, F., op. cit., 146
5. Pringsheim, P., Fluorescence and Phosphorescence, New York, Interscience, 1949.
6. Klick, C.C., and Schulman, J.H., Phys. Rev. 75, 1606 (1949).
7. Seitz, F., Trans. Faraday Soc. 35, 74 (1939).
8. von Hippel, A., Z. Phys. 101, 680 (1936).
9. Williams, F.E., J. Chem. Phys. 19, 457 (1951).
10. Ewald, P.P. and Herman, C., Strukturbericht, Vol. I, page 347, Leipzig, Akademische Verlagsgesellschaft M.B.H., 1931.
11. Jenkins, F.A. and White, H.E., Fundamentals of Physical Optics, page 560 f.f. 2nd. Ed., New York, McGraw Hill, 1950.
12. Stratton, J.A., Electromagnetic Theory, page 490 f.f., New York, McGraw-Hill, 1941.
13. Gillette, R.H., Rev. Sci. Inst. 21, 294 (1950).
14. Longini, R.L., J. Opt. Soc. Am. 39, 551 (1949).

15. Botden, P.J. and Kröger, F.A., *Physica* 15, 747 (1949).
16. Sears, F.W., *Optics*, page 39 f.f., Cambridge, Addison Wesley, 1949.
17. Forsythe, W.E. and Adams, E.Q., *J. Opt. Soc. Am.* 35, 108 (1945).
18. Forsythe, W.E., *Measurement of Radiant Energy*, New York, McGraw-Hill, 1937.
19. Strong, J., *Procedures in Experimental Physics*, page 455, New York, Prentice-Hall, (1943).
20. Victoreen, J.A., *Proc. I.R.E.* 37, 432 (1949).
21. Cartwright, C.H., and Strong, J., *Procedures in Experimental Physics*, page 35 f.f., New York, Prentice-Hall, (1943).
22. Landolt, H.H. and Börnstein, R., *Physikalisch-Chemische Tabellen*, Vol. 5b, page 1512, Berlin, Springer (1935), which quotes: Harada, *Journ. Fac. Sci. Hokkaido Imp. Univ.* 2, 279 (1934). See also: Zambonini, *Zeit. für Krystallographie* 58, 226 (1923).
23. Botden, P.J., *Philips Research Reports* 6, 425 (1951).
24. Kröger, F.A., *Philips Research Reports* 2, 340 (1942).

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